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PROCEEDINGS

OF THE

NINTH

COTTON UTILIZATION RESEARCH

CONFERENCE

Held at

New Orleans, Louisiana

April 30 to May 2, 1969

Agricultural Research Service

UNITED STATES DEPARTMENT OF AGRICULTURE

PREFACE

The Cotton Utilization Research Conference is sponsored annually by USDA's Southern Utilization Research and Development Division to bring the results of cotton research (fundamental, chemical modification, and mechanical processing) conducted by the Division to the attention of representatives of the textile and allied industries and other interested organizations. Presentations at this year's meeting included studies on the use of high-speed photography for elucidating problems in textile machinery operations and the development of new techniques for processing cotton; fundamental studies on the structure and chemistry of cellulose; radiation; wash-wear, durable press, and flame-retardant cotton products; and a report by the Western Utilization Research and Development Division of research on knitted wool fabrics.

These proceedings report in full or in summary the statements presented by the various speakers during the conference and give an account of the discussions following.

C. H. FISHER, Director
Southern Utilization Research and Development Division

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Underscored numbers in parentheses refer to references at the end of each paper. The data presented in the references, figures, and tables are reproduced essentially as they were supplied by the author of each paper.

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WELCOME

by

C. H. Fisher, Director
Southern Utilization Research and Development Division
New Orleans, La.

It is my great privilege and pleasure to welcome you to the Ninth Annual Cotton Utilization Research Conference. Thanks largely to the cooperation and support of our friends in other organizations, all of these conferences have been successful.

We have a good program and distinguished leaders from educational and research organizations serving as general and session chairmen. It is highly gratifying and complimentary that we have such a splendid audience, both in quality and quantity. Bruno Wojcik tells me that we will have over 200 in attendance.

I welcome you also on behalf of George W. Irving, Jr., Administrator, and Fred R. Senti, Deputy Administrator, of USDA's Agricultural Research Service. They regret that they cannot be present. They have asked that their greetings and best wishes be given to you.

We are highly complimented because several of our friends from other countries are attending the Conference. We wish to give a special welcome to Yannick Villegas and Alejandro Lazo, Instituto Mexicano de Investigaciones Technologicas, A.C., Mexico City; and D. Heathcote and J.P. Leaver, Laporte Industries, Widnes, England.

Perhaps you have noted that the names of our official advisers for cotton are listed on the back of the program. I am pleased to note that at least one of them is in the audience. I wish to give our official advisers a special welcome and thanks for their valuable help to the Southern Regional Research Laboratory, headquarters of USDA's Southern Utilization Research and Development Division (SURDD).

Probably most of you know that the principal purpose of these annual Conferences is to report our cotton research promptly and to receive your comments. We hope that you will feel completely free to make comments and suggestions during the Conference and the entire year.

I wish to bring your attention to some of the highlights of the past year.

Our new building has been completed and is in use. This building, with about 30,000 square feet, houses two pilot plants — one for processing cotton mechanically, the other chemically.

The Textile and Clothing Laboratory, which had been located at Beltsville, Md., is now a part of our Southern Utilization Research and Development Division. The work of the Textile and Clothing Laboratory is particularly well known to home economists. This Laboratory, now located on the University of Tennessee Campus, is being operated in cooperation with that University. Ben M. Kopacz, Acting Chief, is doing a good job directing the affairs of this Laboratory.

During the past year, our research conducted in cooperation with many organizations has continued to pay high dividends. Some of our research findings have been adopted by other organizations and used for practical purposes.

The results of our research, both basic and applied, were described last year in 45 patents and some 300 publications and reports. All of these are readily available and, we hope, proving to be helpful to those in research and in the textile industry.

I wish to express thanks to the many individuals contributing to the success of our Conference. Among these are: General Chairman, Roy L. Lovvorn; our several session chairmen; our speakers, including our luncheon speakers, Dave L. Pearce and John A. Cox; our researchers for their valuable work; and other members of the SURDD for their supporting activities.

We hope the Conference will achieve its principal mission of helping cotton meet its competition. I hope participation in the Conference will be rewarding and enjoyable for all of you.

OPENING REMARKS

by

Roy L. Lovvorn
North Carolina State University
Raleigh, N. C.

I am honored at being asked to serve as your General Chairman. I am pleased because I am interested in cotton as a commodity and in seeing its full potential realized in this Nation. I am pleased because I enjoy associating with research people when they are given the opportunity of presenting their new information to an interested public. I am pleased because I have known Dr. Fisher for a long time; because I have a high regard for him and I am always happy to be associated with him and members of his staff.

In 1966 a joint committee of U.S. Department of Agriculture and State Agricultural Experiment Stations developed a long-range plan for agricultural research needs in this country. The plan provided for in-depth task force studies to be made on a number of our leading agricultural commodities. The cotton task force report was released nearly a year ago, and I am taking certain liberties of drawing from it.

Less than 25 years ago cotton accounted for over 80 percent of all fibers consumed by American mills. Today mills use less than one-half as much cotton as manmade fibers. If cotton can capture just half of the natural increases in the fiber market for only the next 2 years through its own research and promotion, there will be $110 million more in cash for American cotton farmers and a need for 900 thousand additional acres.

The greatest impact of the special competition which cotton faces, however, is in the end-use markets for textile products. It is here that individual and industrial consumers choose their textile products, largely on the basis of performance, promotion and price. It is here that the greatest proportion of the synthetic fiber research effort — now estimated at over $149 million annually — is concentrated.

This task force identified four major areas needing more research. They are as follows:

1. To cut costs and losses and increase efficiency in production and processing of cotton.

2. To improve, preserve, and deliver quality in cotton.

3. To develop new and improved cotton products.

4. To facilitate adjustments of people, businesses, and communities.

For the next 3 days you will have an opportunity to hear what the Southern Utilization Research and Development Division is doing about some of these items, especially item 3. We appreciate your presence and we know you will profit from it.

THE FUTURE OF COTTON

by
Preston E. LaFerney
Economic Research Service, USDA
Clemson, S. C.

Future — it's a big word! The future of cotton — it's a big topic! Associated with this topic is a key concept — change. Within this concept lies our challenge as we chart the future for cotton. We must accept change — it is inevitable. But we can affect, or direct, or at least temper, the relevant changes of the future by properly interpreting those of the present. The question is this: Will we read and interpret the winds of change scientifically and then go on to determine and initiate actions which will optimize cotton's position in the future? The dividends resulting from "right" decisions and actions will be great. Those resulting from "wrong" decisions and actions (or inactions) can be catastrophic.

In the beginning, then, let me affirm what I hope is the feeling of each one here associated with the future of cotton. It is an interesting and challenging and rewarding time to be working with cotton.

It would be presumptious of one so new to the industry as myself to try to answer many of the big questions uppermost in our minds concerning cotton's future or even to set a list of priorities for action today. But I can pull relevant factors together and think productively concerning alternatives open to us. And, as I have done this, I can see cotton's future with some optimism, despite some very serious problems. To realize an optimistic future for cotton, there are several critical factors to keep in perspective through coming days. I will call attention to some of these as I see them. I would hope that my remarks may provide not only the keynote of this conference, but also some "food for productive thought" as we in the industry continue to grapple with cotton's problems. My purpose then is to take a brief look at current trends relevant to cotton's future and to relate these to cotton's prospects in general and to our research efforts with cotton in particular.

FUTURE OF TEXTILES

Let us note some tremendously important factors on the plus side for cotton's future and ignore the pressing problems for a moment. Textile fiber consumption continues to increase significantly year by year.

Not only does population continue to increase, but also per capita fiber consumption continues upward. In a recent issue of the *Daily News Record*, under the headline "Textiles Seen Expanding Role in Consumer Living," I found this thought:

> "Higher living standards, expanding population, space age conquest, and new laboratory developments will all contribute to a larger consumption of all types of man-made and natural fibers."

The same general trend is evident on the world scene.

The situation is this: Consumers are continuously "trading up." They are in a position to insist not only in improvements in the quality of products they buy, but also in new products that are constantly being developed. For the textile industry, this has meant and will continue to mean growing markets along with a greater emphasis on quality at all levels. A market oriented textile industry can be thankful for this insistence on better products. The extent to which cotton becomes market oriented will determine the extent to which cotton shares in these expanded markets.

New directions internal to the textile industry also lend optimism to our view of cotton's future. The trend toward larger business units is resulting in greater efficiencies, the results of which are shared by raw fiber suppliers. An improved profit position in the 1960's relative to that of the 1950's is also encouraging. Increasing expenditures for modernization during the past 5 years have provided new technologies, resulting in greater efficiencies.

These are some of the more important factors which inspire optimism for the future of the textile industry, thus for the future of cotton. Our goal for cotton, then, must be to do all we can to capitalize on the opportunities associated with a healthy, expanding textile industry.

FUTURE OF COTTON

As we think of cotton's future as a supplier of textile inputs, both domestic and foreign, several serious problems are immediately evident to dampen the optimism to which I have referred. I have grouped all such problems into three broad categories: (1) Import problems, (2) export problems, and (3) problems of interfiber competition.

The first two problems are obvious to each one here — in fact, all too obvious. Expanding imports for all textiles spell serious trouble for the American cotton, as do continually shrinking exports of raw cotton. Although both problems are well defined, what can be done about them is much less obvious.

Since both the import and the export problems are very deeply interrelated with our national trade policies and since both are sales rather than technical problems, I will only mention them here as having great significance for cotton's future. We must very soon register progress on both fronts. Since I was asked to deal more with the technical issues related to our research programs and to cotton's future, my other remarks will relate to problems of interfiber competition where the technical issues are more relevant.

As we think of interfiber competition and its relation to cotton's future, permit me to make one understatement. We are in trouble. By realizing the truth of this statement, hopefully we can maneuver ourselves into a position to do something about it. Regardless of the developments on exports of cotton and imports of all textiles, interfiber competition undoubtedly is our most serious problem. Although cotton's absolute share of the total domestic fiber market has declined only slightly during the past 5 years, its percentage share of the total has fallen quite rapidly. Just within the past 2 years (1966 to 1968) cotton's percentage share of this market has fallen from almost half the total to just over one-third of the total, on a cotton equivalent basis.

With this competitive situation in mind, it is imperative that we view cotton's future under two alternative conditions: (1) Assuming that a durable-press finish for 100 percent cotton, capable of competing effectively with man-made and blended durable-press fabrics, will be forthcoming in the near future, or (2) assuming that relatively little progress will be made with our durable-press research in the next 5 years. Can anyone deny that cotton's future depends to a very great extent on which condition prevails?

The development of a competitive durable-press finish for all-cotton fabrics in the near future, considering cotton's other desirable qualities, would put much broader smiles on our faces immediately. Not only would it probably disrupt and perhaps reverse the rapid trend toward the use of synthetics, but also would free money now spent on durable-press research for use in the development of other desirable properties for all-cotton products and for research in other areas. Truly, such a development would be most welcome. For this reason, I suggest serious consideration of continued heavy emphasis on research to develop a truly competitive durable-press finish for cotton. This suggestion is made with full realization that the probability of success with this research may be quite low. Several years of past research without producing a satisfactory durable-press finish

should remind us that "it may be some time away yet." But we must continue to search diligently.

There does exist the definite possibility that we may have to compete without a durable-press finish for cotton. For this reason, we must continually raise within the minds of the best thinkers in the industry the question of advisability of researching and promoting blends with synthetics which are favorable to cotton. The word "change" is relevant here. As conditions change, the "right" decision and implied action may change. The question of the advisability of researching and promoting more favorable blends with synthetics admittedly is a tough one. I am simply suggesting that we keep the question open in the midst of our changing competitive position. There are many in the industry who feel that, in the absence of a satisfactory durable-press finish for all-cotton products, the consumer could be offered better blended products to the benefit of cotton's future.

More specifically, they would mention the critical need for information of the following nature:

(1) From the standpoint of cotton and the consumer, what are the optimum blends in various end uses?
(2) In these same end uses, how does blending with synthetics affect the qualities of raw cotton needed for optimum mill performance and for the greatest consumer satisfaction?
(3) What are the behavior patterns of different qualities of cotton in the manufacture of blended yarns and fabrics?

Regardless of the outcome of our research on durable-press finishes, we must continue other established lines of research to keep cotton competitive. In general, I would urge attention to research designed to (1) reduce costs at the farm level and at every stage of processing, (2) increase the efficiency of the marketing system for raw cotton and for cotton products, and (3) maintain and improve cotton's inherent qualities.

Cost reduction — The capacity to produce man-made fibers is expected to further expand during the next few years. In the past, increasing supplies of these fibers have led to decreasing prices and greater competition with cotton. As this trend continues, we must reduce the cost of raw cotton to the mills. Thus, research at the farm level is imperative. Yields per acre must be increased. This may involve development of new varieties; setting of more fruit on the plant; better control of weeds, insects, and diseases; better cultural practices; more efficient farm producing units; and more efficient harvesting and ginning methods.

The general problem of cost reduction at the farm level has been labeled by the National Cotton Council as "a fundamental problem for U. S. cotton," and rightly so. Furthermore, the Council has suggested some specifics as to how we can tackle this problem.

At the various stages of cotton textile manufacturing, research is needed to provide new technologies designed for efficiency. A major aspect of utilization research is involved here. New systems and new machines for handling cotton at reduced costs must be sought. We will hear reports of progress along these lines as this conference progresses.

The aid of computers and modern techniques of studying systems must be enlisted to cotton's advantage. Some research in which I am currently involved suggests that modeling textile processing on the computer to improve the way we lay down cotton mixes and process those mixes can lead to improved efficiency in mill situations. As yet, this tool is largely untapped in our industry.

Research on cost reduction at each economic level must continue to receive considerable emphasis. The decreasing prices of competing fibers dictate this.

Marketing system — Turning our attention to the cotton marketing system, we find other opportunities for improving cotton's future. Ranking high on this list of musts is a means of achieving greater stability in the price of cotton.

Looking backward, we can see that the abnormally high prices paid for cotton during late 1967 and early 1968 have hurt cotton's position. Such volatile prices upset the plans of both producers and users of cotton. Users' confidence in cotton as a dependable and stable input is shaken. Looking forward, attention must be given in our research and policy formulation to ways of achieving greater price stability. Our domestic textile mills must have access to ample supplies of cotton at competitive prices.

Another significant opportunity for improving cotton's competitive position lies in the further development of the very basic idea of market orientation — frankly asking "what does the consumer want?" and "what qualities of cotton and what modifying treatments are required to deliver the product he wants?" This concept must be applied at both the farm and mill level. In this regard, I quote the recent remarks of one textile industry representative:

> "Unless cotton growers and cotton spinners become market oriented and involved in the determination of both present and future uses for the fiber, cotton will suffer 'the same fate as the buggy whip industry.' "

Implementation of this idea will require the development of a feedback of information from the consumer — what he likes and dislikes in a product, hopefully in quantifiable terms. This would assist our utilization laboratory, as well as private industry, to develop new products tailored to consumer wants. It would also strengthen promotional activities for cotton by indicating the particular attributes of cotton to advertise most heavily.

For utilization research, there is another recent, significant trend. That is the great popularity of knitted fabric in apparel items. Indications are that this will continue. Cotton has some special problems competing in this area, I understand, so research designed to improve cotton's performance in knits should be given serious consideration.

We appear to be on the threshold of a satisfactory system of fiber testing with fully automated electronic devices. Research to further develop and refine this system is essential. Developments here are interrelated with efforts to reduce costs of processing, since greater precision in fiber testing will allow a more precise fitting of raw cottons to specific needs in processing, as dictated by demands in the consumer market. These developments also relate to maintenance of a high level of raw cotton quality. An improved description of each bale's quality will contribute to improved production, marketing, and utilization of cotton.

Maintaining and improving quality — It has long been recognized that continuing attention must be given to maintenance of cotton quality if cotton is to remain competitive. Much progress in this area has been made in recent years. Farmers are planting higher quality varieties and, to a great extent, are handling and ginning these varieties so as to preserve the inherent qualities they produce. This is the fruit of research — research that must be continued to seek out better qualities and better information for quality preservation.

Our battles are not completely won in the area of quality, however. With the lack of price differentials or premiums for high quality during the past marketing year, there is producer sentiment for returning to lower quality varieties which hold some promise of slightly higher yields. In the long run, this can mean more trouble for cotton. Also, are we getting back into ginning quality troubles? The wide differentials in recent months in the prices of Middling and Strict Low Middling cotton suggest the possibility. At this point, I again simply raise the question of market orientation. We produce cotton for use by a textile industry which must listen to the consumer in the market place. Therefore, we must deliver quality cotton.

In our research, in our national policies, and in our general attitudes, we must continue to stress cotton as a high-quality product.

General philosophy — Our general philosophy, particularly in research, is of utmost importance to the future of cotton. Earlier I mentioned the concept of change. We must not only accept change, but also stand ready to use it to cotton's advantage. To do this, we must look forward and try to anticipate the problems which we will face over the next 2 to 5 years. We must do this in order to plan research today to meet those needs. In some respects, this takes an adventurous spirit — a willingness to use our best judgment to direct research for anticipated future needs. Because changes occur rapidly in today's world, perhaps more of our research will need to be of a short-run nature — tailored to the needs of decision makers.

In our philosophy, we must give emphasis to a balanced total research program, with continuous attention to priorities in light of current trends and their implications for the future.

Today, from where I stand, it looks like heavy emphasis on a durable-press finish for all-cotton fabrics, a continuing examination of our traditional view of research on cotton-synthetic blends, and as much attention to other research to make cotton competitive as the budget will allow. How will the situation look tomorrow or next year? It may be different, so our philosophy must allow for sudden change of emphasis when it is to cotton's advantage to do so.

Finally, may I remind us that there is power in positive thinking. Do not underestimate this basic truth. With this in mind, we must seek out cotton's strong points through market research and capitalize on them. Let's not forget that cotton still possesses unique desirable characteristics from the consumer's standpoint. These strong points must be promoted in the market place. And remember that other desirable characteristics, such as durable press and nonflammability, perhaps can be developed through properly planned and conducted research. They could have major impact on our competitive position.

The future of cotton? Our situation is serious, but all is not lost. Our opportunities and our challenges are great and interesting and exciting. We can, we must, and we will preserve for cotton the future which it rightfully deserves.

FIRST SESSION: B. F. Tipton, Dan River Mills, Inc., Greenville, S. C., Chairman

OBJECTIVES AND ACCOMPLISHMENTS OF MECHANICAL PROCESSING RESEARCH

by

R. A. Rusca
Southern Utilization Research and Development Division
New Orleans, La.

The United States Department of Agriculture is engaged in three areas of cotton research: (1) Production, concerned with plant breeding, farm cultural practices and ginning; (2) utilization, concerned with increasing present uses and developing new uses for cotton; and (3) marketing, concerned with the orderly movement of cotton into consumer channels.

The Southern Utilization Research and Development Division (SURDD) conducts utilization research to convert cotton into consumer products with new and useful properties. This is being accomplished through basic research on the physical and chemical properties of cotton and applied research on the mechanical processing of cotton into greige goods and the chemical finishing of the goods.

The Division's mechanical processing is conducted in the Cotton Mechanical Laboratory, whose objective is to develop new and improved textile processing methods, techniques, and machinery. Specific lines of research are to: (1) determine the effects of fiber physical properties and the influence of machine variables on product properties and processing efficiency; (2) develop improved products and new products from the various qualities of American cotton; and (3) develop new and improved equipment for processing cotton into textiles.

The research is carried out by a staff of about 50 textile and cotton technologist, engineers, physicists, and textile machine operators. A fully equipped processing plant--actually it is a 1,200 spindle textile mill--enables duplicating the latest processing technology of industry. The research findings, therefore, can be applied in industry with little or no modification.

This is important, because textile mills constitute the sole market for the farmers' cotton (exclusive of the government loan program). The Laboratory's research is intended to show mills how to process cotton at lower cost into higher quality products, and thus make cotton more competitive with man-made fibers at the mill level.

Time does not permit discussing the findings of the various investigations. Briefly, in the past few years the Fiber Property research group has elucidated the effect of length, length distribution, strength, fineness, elongation, and other physical fiber characteristics on the properties of yarns and fabrics. The group has published extensively in this area and on processing organizations to achieve highest production efficiency and lowest manufacturing costs. Current research is directed toward developing improved processing methods and products from lower quality cottons--the so-called "discount" cottons.

The Product Development Investigations has developed cotton stretch yarns and fabrics; durable-press seersucker fabrics for men's, ladies', and children's wear; high-density fabrics for rainwear, tents, tarpaulins; summer weight flight suits for the Navy; and is presently determining the best types and weaves of fabrics for chemical treatments to produce durable-press apparel.

Machinery Development research has produced the SRRL Opener, Opener-Cleaner, Loom Attachment, Granular Card, Fiber Retriever and, this past year, the new Bale-Opener-Blender. Operating under 109 licenses from USDA, 5 textile machinery manufacturers have sold an

estimated $9.3 million of Cotton Mechanical Laboratory-developed equipment to cotton mills. Research is now being directed toward the development of a fundamentally new system for processing cotton from bale to yarn in one operation.

Assuming continued successful research, the Laboratory will furnish industry with new, basic knowledge on the influence of fiber properties on product properties, and with new products and new principles of processing equipment. All of these contribute to increasing the utilization of cotton.

HIGH-SPEED PHOTOGRAPHY IN TEXTILE MACHINERY RESEARCH

by

H. W. Weller, Jr., M. Mayer, Jr., and A. F. Fayette
Southern Utilization Research and Development Division
New Orleans, La.

(Presented by H. W. Weller, Jr.)

Textile machinery research at the Southern Regional Research Laboratory (SRRL) includes the study and evaluation of both conventional and experimental machinery. In investigating the action and interaction of machine components and cotton in process, it is necessary to establish cause and effect relationships. High-speed motion picture photography possesses several characteristics which make it an ideal data-recording system for this purpose. Its most important characteristic is that it allows the detailed examination of time and space relationships.

High-speed photographic equipment in use at SRRL include two 16 mm. rotating prism framing cameras, an electronic control unit, an assortment of interchangeable lenses, and other associated accessories. This equipment is designed to photograph at speeds up to 8,000 pictures per second and to magnify subjects as small as one-half inch wide to the full width of the projected image.

Frequent use has been made of high-speed photographic techniques for solving problems connected with machinery development research. During the development of the SRRL Aerodynamic-Cleaner, high-speed films delineated the flow of cotton and trash through critical areas. These visual studies enabled redesign to obtain more efficient trash removal and smoother flow of fibers past the trash removal area.

The Electrostatic Fiber Fractionator is an experimental device which utilizes an electrical field to separate long and short cotton fibers. High-speed photographs provided data on the movements of the fibers and on the configuration of the electrical field. The pictures provided the information necessary for redesigning the machine to obtain greater production and increased short fiber removal.

High-speed photography was also used to record the motions of individualized cotton fibers in a uniform electrical field. Analysis of the films showed numerous unpredictable fiber actions and revealed the necessity for additional fundamental studies of the action of cotton fibers in electrical fields.

An experimental drafting unit was constructed specifically for studying the basic process of drafting. High-speed films of fibers being drafted revealed a slip-stick phenomenon and clearly showed that the fibers tend to "spring" back to their original shape as they are released from the restraining effects of adjacent fibers.

A photographic study of the experimental SRRL Ringless Spinning machine was

undertaken to investigate the movements of the fibers at the end of the yarn in the piecing-up area. Analysis of these films suggested modifications which were used to improve the performance of the apparatus.

High-speed motion picture photography frequently has been used to study conventional processing machinery and processes to aid in improving the process or equipment. For example, a study of the fiber opening efficiency of the lickerin of a conventional textile card showed that even when the lickerin is carrying a light load the fiber tufts on the lickerin surface were much larger than are considered ideal for efficient carding.

Films of the cleaning cylinder of the Shirley Analyzer showed a much smaller average tuft size than those on the card lickerin. Information on the efficiency of fiber opening and fiber movement observed from the films of the card lickerin and the Shirley Analyzer was used in the development and design of the SRRL Pre-Carder.

Photographs of the removal of the web from the doffer cylinder by the card doffer comb revealed that when the comb is at its lowest point the web appears to be held together by only a few fibers. It also revealed a snapback action of some fibers which are held by the doffer, extended by the comb, and then released by the comb. It was felt that this action contributes to nep formation, although conclusive evidence was not obtained.

Textile machinery research at the Southern Regional Research Laboratory involves a continually changing array of technical problems. Most of these problems can be solved by relatively simple measurements. For many, however, high-speed photography provides the best, and sometimes the only, method for obtaining a solution.

A COMPARISON OF VARIOUS INDICES FOR MEASURING FIBER ORIENTATION

[SUMMARY]

by

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(Presented by J. Simpson)

It is well known that to spin a smooth, strong yarn the fibers must be as parallel as possible. However, up to several years ago parallelization could not be measured because of lack of practical techniques.

The introduction of new and automated processing systems has prompted interest in measuring both fiber hooks and parallelization, commonly referred to as fiber "orientation." Most of the recently developed techniques for measuring fiber orientation involve procedures for clamping and combing the fibers. From these procedures a number of indices for measuring both fiber hooks and parallelization have been proposed. For example, the cutting ratio[1/], fiber hook index[2/], and percent E[3/] from the modified Lindsley technique are all relative measures

[1/] Simpson, J. Sliver direction, hooked ends have significant effect on the parallelization of cotton fiber. Textile Bull. 87(7): 39-42. 1961.
[2/] Leont'eva, I. S. Problem of fiber straightening during sliver preparation. Technol. Textile Indus., USSR 2: 57-63. 1964.
[3/] DeLuca, L. B. An evaluation of hooked fibers in cotton sliver on a relative basis. Textile Res. Jour. 35: 858-861. 1965.

of fiber hooks and each has been found to correlate well with fiber hooks as obtained with the tracer fiber technique. Indices for measuring fiber parallelization obtained with the modified Lindsley technique are the coefficient of relative fiber parallelization (percent weight gripped)[2] and the combing ratio[4]. Both are relative measures of fiber parallelization; the former is a direct measure and the latter is an indirect measure.

A clamping and combing method has also been developed to measure fiber parallelization in terms of the projected mean length and fiber hooks in terms of ideal random hooks per fiber[5]. Both are absolute measures; that is, the ideal random hooks per fiber measurement is independent of the length distribution of the cotton.

This paper reports on an evaluation undertaken to determine the practical usefulness of the various indices for measuring fiber hooks and parallelization. The cutting ratio was compared with the ideal hooks per fiber, and the percent weight gripped was compared with the projected mean length. Measurements were made on slivers produced with variations in prespinning processing variables such as drafting direction, sliver weight, and carding rate.

Percent weight gripped versus projected mean length--A comparison of the projected mean length with percent weight gripped showed that each was equally effective in evaluating fiber parallelization and processing performance. Projected mean length is preferred when measuring fiber parallelization of different cottons since it is an absolute rather than a relative measure.

Cutting ratio versus hooks per fiber--A comparison of the cutting ratio with hooks per fiber showed that the latter index was not as effective in determining the "hooking" configuration in slivers as the former index or as the fiber tracer technique. By using the cutting ratio, it was possible to determine that in some instances a fibrous strand with unparallelized fibers contained relatively few hooks; whereas this relationship could not be determined by use of the hooks per fiber index since hooks per fiber and projected mean length are inversely related, by definition.

The cutting ratio showed that both majority and minority hooks were reduced more when they trailed into the drawing process than when they led. However, when the hooks per fiber were used, erratic and inclusive results were obtained. It was also found that while the overall fiber parallelization, such as unaligned fibers and fiber crimp, had an effect on the cutting ratio, especially for card sliver, it had a much greater effect on the hooks per fiber measurement. It, therefore, appears that the hooks per fiber concept, at this stage of the evaluation studies, has limited application for determining the "hooking" characteristics of a fibrous strand.

Therefore, at our present state of knowledge it appears that the projected mean length and the cutting ratio or similar index should be used for obtaining measurements of fiber parallelization and hooks, respectively.

DISCUSSION

QUESTION: Is there any material difference in the processing behavior of discount cottons and the cottons reported on in your paper?

MR. SIMPSON: Low Micronaire cottons, as represented by discount cottons, tends to load the card cylinders. Research has shown that it was preferable to increase cylinder speeds to prevent loading than to experiment with other card adjustments.

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[4] Lindsley, C. H. Measurement of fiber orientation. Textile Res. Jour. 21: 39-46. 1951.
[5] Tallant, J. D., Pittman, R. A., and Patureau, M. A. Simple length measurement leads to reduced end breakage. Textile Bull. 94(5): 30-32, 34-35. 1968.

DRAWING FRAME VARIABLE EFFECTS ON YARN PROPERTIES AND PROCESSING PERFORMANCE

[SUMMARY]

by

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(Presented by J. E. Sands)

Recent trends in the drawing process have been toward more doublings, higher drafts, higher speeds, and heavier slivers. There is a scarcity of published information on the effect of these processing variables on processing performance, except for one comprehensive study[1/]. The drawing process has been shown to have important effects on fiber orientation and hooks; however, sliver direction and sliver weight were the only major variables evaluated. The combination of drawing frame variables which will produce sliver of best uniformity may not be the best for optimum fiber orientation, minimum fiber hooks, or utilization of maximum effective fiber length.

This investigation was undertaken to determine the combination of drawing frame processing variables which would result in a sliver of best "overall" quality as reflected in ultimate yarn properties and spinning performance. A mill-type cotton mix of 20 percent Eastern, 38 percent Western, and 42 percent Memphis territory growth was used. The stock was carded at 20 pounds per hour on a card equipped with a crush roll attachment and was made into 55, 65, and 80 grain per yard sliver.

Three "blocks" of tests were made. Each weight of sliver was processed through first and second drawing: (1) with each of three "normal" drafts (with equivalent doublings) to evaluate the effects of sliver weight, total draft and doublings, back roll setting, and top draft roll spacing; (2) with each of three "experimental" draft distributions (with equivalent doublings) to evaluate the effects of draft distribution; and (3) with added weight on the back roll using the draft of 10 with 10 doublings to evaluate the effect of this added weight.

Evaluations were made of yarn breakage during spinning, skein and single strand breaking strength, single strand elongation at break, single strand evenness, and thick and thin places and imperfections.

It was determined that increases in sliver weight were associated with decreases in yarn strength and evenness, and with increases in yarn imperfections and end breakage during spinning.

Experimental draft distributions at drawing produced somewhat less yarn strength, slight decreases in yarn evenness, somewhat fewer imperfections and significant improvements in end breakage during spinning.

Investigations of drafts and doublings showed that the best yarn strength was achieved with the eight draft and eight doublings. There were slight effects on yarn evenness and imperfections. End breakage during spinning was reduced appreciably with the 10 draft and 10 doublings.

Opening the top draft roll spacing resulted in improvements in yarn strength and end breakage in spinning, with no appreciable effect on yarn evenness or imperfections.

Opening the back rolls was associated with reductions in yarn strength, yarn evenness, and end breakage during spinning and with increases in yarn imperfections.

[1/] Bogdan, J. F. An exploration of roller drafting. Textile Bull. 88(2): 35-39. 1962.

There was some evidence that the experimental roll weighting increased yarn imperfections and thick places and reduced the thin places. However, the data were not statistically significant, probably because of the inherently large variation in these types of measurements. There was no correlation between normal or experimental back roll weighting and end breakage.

Using a four over five drafting system on the drawing frame, the best spinning conditions and yarn properties were obtained by using a combination of: (1) A lightweight sliver, (2) normal draft distribution, (3) eight draft and eight doublings, (4) open top roll spacing, (5) closed back roll setting, and (6) either with or without added weight on the back rolls.

DISCUSSION

QUESTION: Has any work been done using crush rolls at the draw frame?

MR. SANDS: Research has not included crush rolls.

SECOND SESSION: W.J. Hamburger, Fabric Research Laboratories, Inc., Dedham, Mass., Chairman

ATMOSPHERIC AND CHEMICAL TREATMENT EFFECTS ON COTTONS VARYING IN INITIAL PROPERTIES [1/]

by

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and

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(Presented by Z. A. Henry)

ABSTRACT

Six cotton varieties selected for their wide range in physical properties were exposed to treatments of five combinations of relative humidity and temperature, to surface treatment by boiling in alcohol, and to extensibility alteration by treatment in 22 percent NaOH. Each cotton variety-treatment combination was tested for moisture regain, density, x-ray angle, tenacity, elongation, impact strength, length, fineness, immaturity, and alkali centrifuge value. Surface properties were investigated by determining the coefficient of friction.

The results showed that cellulose crystallinity was affected by high temperature and humidity, boiling in alcohol, and by NaOH treatment. Cotton fibers were initially damaged by high temperature and low humidity, especially when the two were in combination. The friction data were extremely variable and the coefficient of friction seemed to be dependent upon the normal force.

INTRODUCTION

Characterization of cotton has long been the object of those who would attempt to predict the fiber behavior in mill processing and to project the end use value of the fibers. Another more recent problem has been the alteration of the fiber character, intentionally or otherwise, which would affect its performance. This alteration might be either before, during, or after processing and would usually cause eventual detriment to the fiber and to end product value. The purpose of this investigation was to discover more about how some of the atmospheric, chemical, and physical alterations relate to fiber character and processing. This paper deals only with the atmospheric and chemical effects.

Six cotton varieties selected for their wide range of properties were studied (table 1). The cottons and their treatments in order are given in table 2.

Chemical alteration of and atmospheric effects on the mature fiber occur from

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[1/] A report of work done under contract with U.S. Department of Agriculture and authorized by the Research and Marketing Act. The Contract is being supervised by the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

Table 1. — The six cotton varieties used with location grown and some of the physical property values

Variety	Location grown	X-ray angle		Tenacity 1/8 in. gage	Elongation	Toughness	2.5 pct. span length	Fineness	Immaturity
		40 pct.	50 pct.						
		Degree	Degree	G./tex	Percent	G./tex	Inches	$Mm.^{-1}$	$Mm.^{-1}$
Cal 7-8	Shafter, Calif.	29.9	26.6	22.1	6.2	0.69	1.07	446	28
Deltapine smooth leaf	Stoneville, Miss.	38.2	34.7	19.1	9.0	.86	1.15	458	35
Acala 4-42	Shafter, Calif.	33.5	30.2	21.8	7.8	.85	1.11	516	48
Stoneville 7A	Stoneville, Miss.	34.9	31.9	17.6	7.3	.64	1.15	488	46
Pima S-2	Tempe, Ariz.	29.8	26.9	30.3	9.0	1.37	1.36	495	34
Lankart 57	Lubbock, Tex.	40.6	36.7	16.4	8.7	.71	.99	552	64

Table 2. — Fiber treatments and the measured fiber properties

Chemical and atmospheric treatments	Fiber Properties measured
35 percent RH 72°C. — 2 min.	Density
65 percent RH 72°C. — 2 min.	Moisture regain
80 percent RH 72°C. — 2 min.	X-ray
35 percent RH 180°C. — 2 min.	Tenacity (T_1)
65 percent RH 180°C. — 2 min.	Elongation (E_1)
Alcohol boiled — 3 hr.	Toughness
22 percent NaOH	Impact strength
Control	50-percent span length
	2.5-percent span length
	Fineness (A)
	Immaturity (D)
	ACV
	Friction[1/]

[1/] Friction measurements were made on the control, NaOH samples and samples boiled in alcohol.

weathering in the field before harvest (5), in the gin by heat and moisture treatments (4, 6, 15, 19), in storage from internal heat generation and moisture changes, and from various chemical alterations surrounding processing, all of which affect end use value (1, 16, 18). Selection of the atmospheric and chemical treatments for the cottons of this investigation were made that might simulate conditions to which fibers could be exposed under actual situations as they moved from the field to the end product. A treatment where wax was removed from the fibers by boiling in alcohol was made to test changes in surface character. Structural alteration that would permit a test of the effects of altered extensibility was made by a treatment in a 22 percent solution of NaOH.

MATERIALS AND METHODS

Sample preparation. — In 1964, 10 cotton varieties were grown especially for this investigation by the U.S. Department of Agriculture (USDA), Agricultural Research Service (ARS), Crops Research Division (CRD), and Cotton and Cotton and Cordage Fibers Branch. From these 10 lots, the six which showed the widest range of characteristics were chosen and are given in table 1.

The raw stock sample of 15 to 25 pounds was thoroughly blended. Subsamples were prepared for testing by preparation of a 50 g. multiple card web made by passing the cotton once through a granular card. The sample was

collected in lap form on a drum so that the resulting lap was approximately 60 inches long and 8 inches wide consisting of 32 layers of card web as described by Landstreet and others (13).

Treatments. — The atmospheric treatments of table 2 were selected because they represented combinations of moisture and temperature which might be found, either in nature or in ginning, across the Cotton Belt. The cotton was conditioned for at least 24 hours at the specified humidity in a 72°F. atmosphere before being heat treated. The heat treatment was made at 72° or 180°C. by placing one layer of the lap for 2 minutes between grooved heavy aluminum plates in an oven that had been previously heated to the required temperature. Thermocouple measurements showed that less than a 20 second lag existed between the temperature of the plates and the temperature in the center of the sample from the time the sample was placed between the plates.

Another treatment consisted of boiling the cotton in alcohol for 3 hours. This changed the fiber surface by removing part of the wax. Fiber extensibility was affected by still another treatment in a 22 percent NaOH solution. The sample was saturated for 1 hour in a 0.4 percent wetting solution of Triton at 86°F. before being treated for 30 minutes in NaOH at the same temperature. The NaOH solution was removed from the samples by a flowing bath of tap water at 86°F. The sample was neutralized in a 1.0 percent solution of acetic acid for 5 minutes. After rinsing, the excess water was removed by blotting with paper towels; the sample was dried at 40 percent RH before being conditioned at 65 percent RH.

Testing methods. — Tests which were made on each sub-sample are shown in table 2. Standard instruments and test methods were used for all fiber properties except those for which no standard existed. Where no standard existed but proved procedures have been published, they were used. No adequate published procedures existed for impact tests and surface friction; therefore, instruments and methods were developed especially for these measurements.

Each fiber property was measured as described below:

Fiber density was obtained by the procedure described by Orr and others (17) by using a density-gradient column.

Moisture regain was determined by the method of American Society for Testing Materials (ASTM) Designation D 629-59T.

X-ray diffraction patterns were recorded on films exposed on conventional equipment and evaluated on a modification of the densitometer described by Krowicki and Ewald (11). The modifications consisted of an adaptation that permitted the densitometer output to be amplified and recorded on a strip chart recorder. The data, except as shown in table 1, presented 50 percent x-ray angle [see Duckett and Tripp (3)].

Strength and elongation were determined with the Stelometer at 1/8 in. gage length. A Stelometer especially adapted for high elongation specimens was used for the cottons treated with NaOH.

Toughness was determined from the Stelometer values (20) and was one-half the strength times elongation; $(T_1 \times E_1)/2$.

Impact strength was determined from a device especially designed for this test (fig 1). It was equipped for Pressley clamps at 1/8 in. gage length. The force was transmitted to a cantilevered bar, the deflection of which was sensed by a differential transformer. The resulting signal was amplified and recorded on a strip chart. The

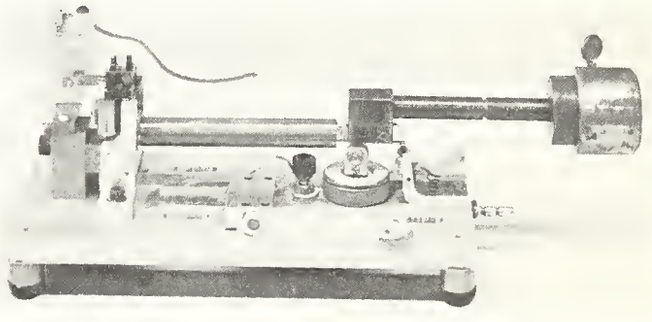

Figure 1. — Impact strength tester for cotton fibers.

time to break for this method, with a specimen adequate for a Stelometer type break was approximately 1/80 second. To insure that the breaker and strip indicator were providing correct information, the breaker was equipped with a dashpot which, by means of a screw adjustment, permitted a large variation in the rate of application of force on the specimen. The variation in the time to break with this modification was from greater than 1 second to less than 1/100 second. Within the range of breaking speeds used in the experiment, the instrument and equipment error was within the limits expected of cotton fiber strength tests.

Length. — Fifty and 2.5 percent span lengths were determined on a digital Fibrograph. The small samples obtained from some of the treatments required that the specimens be prepared by the hand-combed procedure as described in the method of ASTM Designation D 1447-66.

Fineness and immaturity were determined from the Arealometer. The values quoted are the specific area, (A) and the immaturity, (D) as described by Hertel and Craven (10).

Alkali Centrifuge Valve (ACV) was evaluated by the technique developed by Marsh and others (14). An increase in ACV from established control values is considered to be a measure of damage (12) although there are initial differences in ACV among cottons that cannot be attributed to fiber damage.

Fiber friction was determined from equipment especially constructed for this experiment (fig 2). The stand used in specimen preparation is shown in the foreground. The specimen was prepared by placing a bundle of approximately 5 mg. of fiber tightly over a flat surface. The specimen, when mounted on the instrument, could be pressed either against another specimen of fibers, similarly mounted, or against a plane glass or steel surface mounted in the same position that the second specimen would have been placed. This permitted fiber to fiber or fiber to plane surface measurements. The instrument was equipped to provide a force normal to the specimen to specimen or specimen to plane surface contact which could be varied by a dial adjustment. A second dial adjustment could vary the force perpendicular to the normal force. After setting a specified normal force, the force

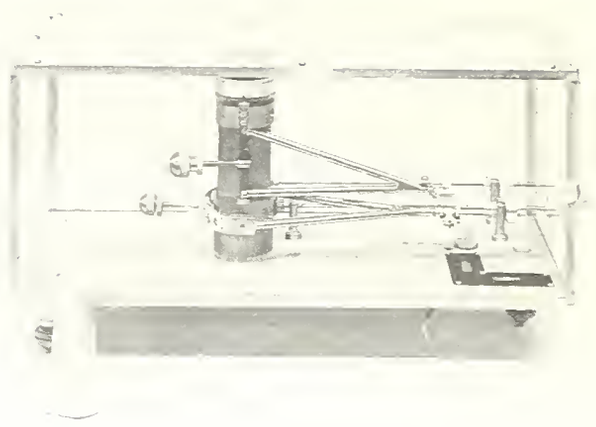

Figure 2. — Friction meter for determining coefficient of friction of fibers.

perpendicular to the normal force was varied until the two surfaces moved with respect to each other. The coefficient of friction was taken as the ratio of the tangential force to the normal force.

A second method consisted of a horizontal plane placed on a disc rotatable about a horizontal axis upon which 1 cm. square cotton pads were tested over a wide range of loads. The disc was rotated until the cotton pads began motion and the coefficient of friction determined from the angle of response.

RESULTS

Internal structure changes. — Density, moisture regain, and x-ray diffraction patterns have been considered to be characteristics of fibers which relate to the internal structure. Density is related to the degree of crystallinity, the crystalline form, and the state of amorphous cellulose. Moisture regain is also affected by the crystallinity in that the valence forces are less saturated in the amorphous material. In turn, x-ray diffraction patterns provide information on the orientation of the crystals. Thus, values in table 3 show that the crystallinity is greatly altered by the NaOH treatment. Crystallinity is not greatly affected by any of the other treatments except the 180°C. temperature. One possible exception is the effect of the high humidity treatment as indicated by the density. Internal changes

Table 3. — Density, moisture regain, and x-ray angle for each of the six varieties and eight treatments with the significance at the 5 percent level [1/] [2/]

Modifications	Cal 7-8	Deltapine SL	Acala 4-42	Stone-ville 7-A	Pima S-2	Lankhart 57
			Density gm./cc.			
Control	1.550A	1.544D	1.546B	1.546B	1.546A	1.547C
35 pct. RH — 72° C.	1.549A	1.545CD	1.546B	1.546B	1.546A	1.546CD
65 pct. RH — 72°C.	1.548AB	1.545CD	1.545C	1.545C	1.545A	1.546DE
80 pct. RH — 72°C.	1.547B	1.543E	1.543D	1.543D	1.544A	1.544F
35 pct. RH — 180 °C.	1.549A	1.548A	1.548A	1.547A	1.548A	1.549A
65 pct. RH — 180 °C.	1.550A	1.547B	1.547A	1.546B	1.547A	1.548B
Alcohol boiled	1.548AB	1.546BC	1.545C	1.544C	1.545A	1.545E
22 pct. NaOH	1.522C	1.516F	1.519E	1.518E	1.522B	1.514G
			Moisture regain percent			
Control	7.31B	7.13B	7.48B	7.56B	7.13CD	7.40BC
35 pct. RH — 72° C.	7.26B	7.12B	7.40B	7.44B	7.06D	7.28C
65 pct. RH — 72°C.	7.28B	7.13B	7.41B	7.47B	7.18CD	7.35BC
80 pct. RH — 72°C.	7.38B	7.19B	7.37B	7.52B	7.27BC	7.43BC
35 pct. RH — 180 °C.	6.80C	6.68C	6.93C	6.93C	6.64E	6.98D
65 pct. RH — 180 °C.	6.84C	6.64C	6.92C	6.82C	6.69E	6.89D
Alcohol boiled	7.36B	7.26B	7.53B	7.59B	7.35B	7.52B
22 pct. NaOH	10.40A	10.31A	10.58A	10.53A	10.21A	10.27A
			50 percent x-ray angle			
Control	26.6B	34.7A	30.2BC	31.9A	26.9B	36.7AB
35 pct. RH — 72°C.	27.8AB	34.2A	31.1ABC	30.9A	27.8AB	34.8C
65 pct. RH — 72°C.	28.3AB	36.1A	32.2AB	30.9A	29.2A	35.8BC
80 pct. RH — 72°C.	28.7A	35.9A	32.7A	30.2A	27.4B	35.3BC
35 pct. RH — 180 °C.	27.9AB	34.9A	31.9AB	30.6A	28.5AB	37.9A
65 pct. RH — 180 °C.	29.6A	35.5A	32.5A	30.7A	27.3B	35.6BC
Alcohol boiled	28.3AB	35.3A	29.0C	30.1A	27.1B	35.7BC
22 pct. NaOH	24.2C	30.5B	26.8D	25.2B	21.1C	27.4D

[1/] Each entry is the average of four readings.

[2/] Those means in a given column followed by the same letter are not significant at the 5-percent level.

induced by the treatments shown in table 3 possibly may be related to the external physical properties. Comparison of table 3 with table 4 shows that, when the means of all varieties are combined, significant differences exist between certain treatments that did not exist in any one of the tested varieties. This may be due to the accentuation in the combined data of nonsignificant trends in the data for the individual varieties. This seemed to be true of almost every fiber property tested.

The Duncan's multiple range analysis of the combined data for each variety and each property (table 5) shows that there was a significant difference among the property means of almost all varieties for every property [see Henry and others (7)]. This is as would be expected since the cottons were initially selected for their wide variations in fiber properties. Further analysis showed that the NaOH treatment affected each of the other measured fiber properties significantly (table 4). This is the expected result since the mercerization process chemically affects the cellulose crystallinity and orientation.

The 80 percent RH and 72°C. treatment decreased the density of each variety. However, this did not seem to affect the other properties measured.

Table 4. — Treatment means for each fiber property and the significance at the 5-percent level[1/]

Treatment	Density	Moisture regain	X-ray angle	Tenacity	Elongation	Toughness
	G./cc.	Percent	Degrees	G./tex.	Percent	G./tex.
Control	1.5464C	7.34BCD	31.15BCD	21.21C	7.65B	0.807B
35 pct. — 72°C.	1.5461C	7.26D	31.09CD	21.21C	7.74B	.815B
65 pct. — 72°C.	1.5456D	7.30CD	32.08A	21.12C	7.61B	.803B
80 pct. — 72°C.	1.5440E	7.36BC	31.69ABCD	21.12C	7.69B	.808B
35 pct. — 180°C.	1.5481A	6.83E	31.95AB	20.39D	7.53B	.764B
65 pct. — 180°C.	1.5476B	6.80E	31.85ABC	20.47D	7.45B	.760B
Alcohol	1.5456D	7.44B	30.92D	22.22B	6.88C	.763B
NaOH	1.5186F	10.38A	25.85E	23.35A	17.88A	2.088A

Treatment	Impact	50-percent span	2.5-percent span	Fineness	Immaturity	ACV
	G./tex.	Length in.	Length.in.	Mm.$^{-1}$	Mm^{-1}	
Control	18.62BC	0.505A	1.128A	498.0A	44.7AB	206.7BC
35 pct. — 72°C.	18.63BC	.507A	1.127A	499.6A	46.6A	208.2B
65 pct. — 72°C.	18.64BC	.507A	1.126AB	500.5A	46.0AB	207.3BC
80 pct. — 72°C.	18.68BC	.506A	1.128A	498.7A	45.9AB	207.8B
35 pct. — 180°C.	17.76D	.493B	1.120B	500.8A	44.8AB	211.7A
65 pct. — 180°C.	17.93CD	.494B	1.120B	501.2A	43.8B	210.6A
Alcohol	19.09B	.475C	1.106C	489.8B	32.7C	206.1C
NaOH	24.18A	.450D	.979D	366.0C	10.9D	197.0D

[1/] Those means in a given column followed by the same letter are not significantly different at the 5-percent level.

Table 5. — Fiber property means for each cotton variety and the significance at the 5 percent level [1/] [2/]

Variety	Impact	Tenacity	Elongation	Toughness	50 percent span	2.5 percent span
	G./tex	G./tex	Percent	G./tex	Length in.	Length in.
Cal 708	20.08B	22.42B	6.97E	0.810D	0.519B	1.052D
DP-SL	17.67D	19.72D	10.02A	.990B	.485D	1.114B
A 4-42	18.94C	21.37C	8.70C	.954B	.502C	1.804C
St. 7A	15.95E	18.57E	7.85D	.740E	.472E	1.115B
P. S-2	27.01A	29.03A	9.22B	1.336A	.583A	1.302A
L 57	15.48E	17.19F	10.07A	.876C	.392F	.958E

Variety	X-ray angle	Density	Moisture regain	ACV	Fineness	Immaturity
	Degrees	G./tex	Percent		Mm.$^{-1}$	Mm.$^{-1}$
Cal 7-8	27.68D	1.5453A	7.58C	191.5E	431.9F	25.4E
DP-SL	34.62A	1.5416E	7.43D	201.7D	441.9E	29.5D
A 4-42	30.80B	1.5421D	7.70AB	212.2B	502.0B	47.1B
St. 7A	30.05C	1.5418DE	7.73A	210.4C	479.6D	41.6C
P. S-2	26.90E	1.5431B	7.44D	200.4D	484.2C	28.6D
L 57	34.89A	1.5425C	7.64BC	255.3A	551.3A	64.4A

[1/] These are the means within a variety of all the modifications.

[2/] Those means in a given column followed by the same letter are not significantly different at the 5-percent level.

The two treatments at the high temperature (180°C.) caused the moisture regain to be significantly reduced. The change in internal structure indicated by this reduced moisture regain definitely affected the tenacity of the fibers. The 35 percent RH and 180°C. treatment usually caused the most detriment. For most varieties both elongation and toughness were reduced by the high temperature treatments; however, the reduction was not significant at the 0.05 level.

Atmospheric treatment effects. — The small reduction in the impact strength due to the atmospheric treatments was not significant for the individual varieties except for the 35 percent RH — 180°C. treatment on Pima S-2 variety. When the data for all varieties were combined (table 4), the impact strength showed a significant difference due to 180°C. heat treatments.

Also, the 50 percent span length was significantly affected only at the 35 percent RH — 180°C. treatment on Pima S-2. However, for the means of all the varieties combined, the 50 and 2.5 percent span length showed significant decreases for both high temperature treatments.

Fineness was affected by the atmospheric treatments only with Cal 7-8 which increased with the 65 percent RH — 72°C. treatment and Acala 4-42 which decreased for the 65 percent RH — 72°C. and 80 percent RH — 72°C. treatments and increased for the 35 percent RH — 180°C. treatment.

The atmospheric treatment did not significantly affect the immaturity value, (D) of the Acala 4-42, Stoneville 7A, and Lankart 57 varieties. Cal 7-8, Deltapine Smooth Leaf, and Pima S-2 showed appreciable scatter in these data.

The damage from the atmospheric treatments as indicated by the alkali centrifuge value had no particular pattern from one cotton to another except for the high temperature treatments. The 35 percent — 180°C. treatment gave significantly higher ACV on Cal 7-8, Deltapine Smooth Leaf, Acala 4-42, and Pima S-2, with Pima S-2 showing the most damage. The varieties that varied significantly in immaturity were in this same group. Data for all varieties combined gave significantly higher ACV for the high temperature treatment.

Effects of wax removal. — Boiling in alcohol removed much of the surface wax. The effect on the surface was observed in the fineness, (A) and the immaturity, (D) values. The A value was lowered significantly on all except Cal 7-8 and Pima S-2 and the D value was lowered significantly for all varieties. These (A and D) are indirectly sensitive to surface characteristics. This is a similar effect to adding a surface roughner that produces an apparent channeling in the Arealometer cotton plug and artifically reduces A. The elongation, E_1, was lowered for each variety while there was an increase in tenacity, T_1 for each variety except Pima S-2. This was probably due in part to better holding in the Pressley jaws (less slippage). It is interesting to note that there is very little change in the toughness value, $(T_1 E_1)/2$, which is an indication of the energy to break. A reduction in length values was noted in all varieties treated with alcohol. This reduction was significant for four varieties (Acala 4-42, Stoneville 7A, Pima S-2, Lankart 57) for the 50 percent span length and for three varieties (Deltapine SL, Stoneville 7A, Lankart 57) for the 2.5 percent span length. This reduction in length was probably accentuated by the breaking of fibers during the combing process in specimen preparation. Boiling in alcohol decreased the density for Acala 4-42, Stoneville 7A, and Lankart 57 and increased it for Deltapine SL. The reduction may have been due to an increased volume of the fiber during boiling (possibly due to swelling of the lumen) which was not penetrated by the solution of the density column. It is especially interesting to note that these significant density effects were on the varieties with higher initial immaturity values.

Convolution effect from NaOH. — The NaOH treatment caused a decrease in the x-ray diffraction angle for all varieties. The difference between the maximum for the control was 10.17 units, but for the NaOH modification was only 7.38 units. This decrease in spread of 2.79 units indicated some loss of convolutions but not a complete loss. Conversion from cellulose I to cellulose II was shown to be complete by analysis of the x-ray pattern.

Friction measurement. — The change in surface properties due to the treatment by NaOH and by boiling in alcohol was determined by the measurement of the coefficient of friction of cotton to cotton, cotton to stainless steel, and cotton to smooth glass on the Friction Meter of figure 2 previously discussed. Friction studies in this laboratory before these experiments had indicated that the frictional values obtained from sliding samples down a simple inclined surface correlated very highly with the air-flow fineness value. This led to the conclusion that the coefficient of friction must vary with the normal force at each contact as previously reported by Bowden and Tabor (2). Table 6 shows the averages for each variety-treatment combination and cotton-surface combination where the normal load was standardized at 6 g. on a circular area of 0.307 in. diameter.

The statistical analyses of these data have shown the following significant differences. Cotton to smooth glass differences between treatment means were significant but the differences between variety means were not. Cotton to stainless steel differences between treatment means were significant but the differences between variety means were not. Cotton to cotton differences between both variety means and treatment means were significant. These results seemed to be greatly affected by difficulty in perfecting specimen preparation and experimental techniques which could bring adequately reproducible results.

This was indicated by the fact that the analyses of variance always showed a significant difference due to replication.

There was a large variation among readings within a given specimen. Cotton to cotton seemed to give the widest scatter among readings of the same specimen but more plausible overall results. Cotton to glass and cotton to stainless

Table 6. — Coefficient of friction of fibers from six cotton varieties and four treatments for three methods of testing with the friction meter.

Treatment	Cal 7-8	Deltapine SL	Acala 4-42	Stoneville 7-A	Pima S-2	Lankart 57	Treatment mean[1/]
			(a) Cotton to smooth glass				
Control	0.122	0.111	0.125	0.127	0.113	0.113	0.118
Alcohol	.105	.130	.114	.114	.120	.125	.118
NaOH	.095	.103	.102	.104	.097	.102	.100
Variety mean	.107	.115	.114	.115	.110	.113	
			(b) Cotton to stainless steel				
Control	.228	.215	.231	.218	.239	.224	.226
Alcohol	.242	.230	.241	.248	.241	.225	.238
NaOH	.226	.226	.221	.233	.223	.231	.227
Variety mean	.232	.224	.231	.233	.234	.227	
			(c) Cotton to cotton				
Control	.203	.201	.186	.229	.171	.224	.202
Alcohol	.230	.230	.255	.243	.229	.265	.242
NaOH	.204	.201	.200	.198	.182	.209	.199
Variety mean[1/]	.212	.211	.214	.223	.194	.233	

[1/] Significantly different at 1-percent level: Modification means within test methods (a), (b), and (c); variety means within test method (c).

steel seemed to vary less among readings of the same specimen but seemed to vary just as much from specimen to specimen as the cotton to cotton measurements. This led to the hypothesis that the distribution of the number and intensity of the contracts were more constant from one measurement to another within any one specimen but varied among specimens. However, the distribution of values for the fiber to fiber surfaces covered a much wider range from one measurement to another within any one specimen but varied no more from specimen to specimen than did the cotton to plane surface measurements.

The results of the friction determination by the inclined plane method where the horizontal plane was attached to the rotatable disc are shown in the graph of figure 3 for continuous runs. Continuous runs were used to ascertain whether the log-log plot was linear as claimed by Bowden and Tabor (2). It was concluded that it was only approximately linear. Figure 3 shows that the cotton boiled in alcohol has a lower coefficient of friction than the untreated. From the apparent roughness of the alcohol treated cotton along with the difficulty in processing it, one would predict that the alcohol treated should have the highest coefficient of friction.

Because of the difficulty in obtaining consistent friction data, further work was initiated which dealt with surface properties in another way. Some of the developments have been reported by Hertel (8, 9).

CONCLUSIONS

This investigation has led to the following conclusions for the varieties to which treatments were applied.

1. Crystallinity was increased with high temperature treatment and was decreased by

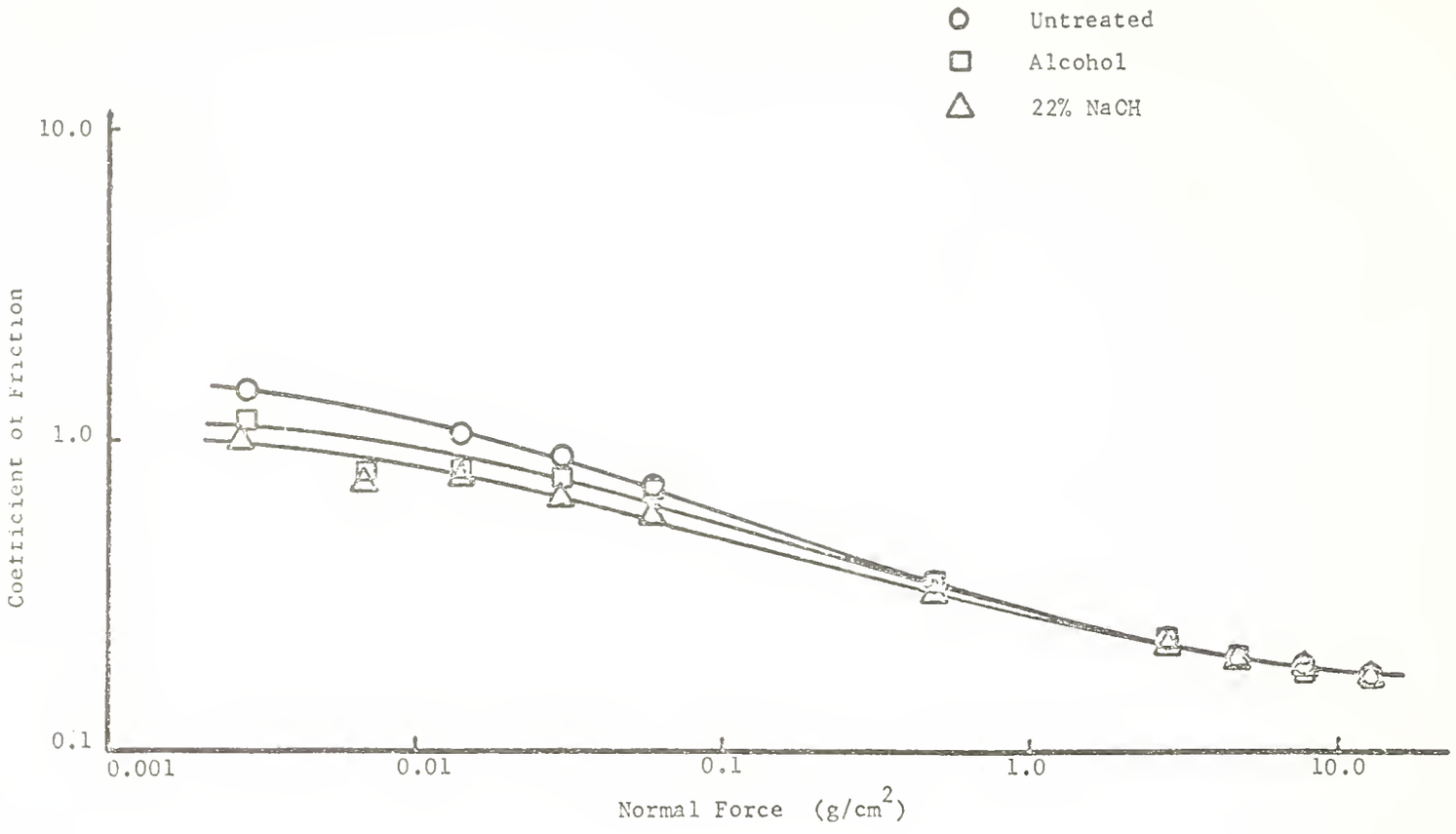

Figure 3. — Coefficient of friction versus normal force over a wide range of normal forces for Cal 7-8 using the inclined plane method.

high humidity treatment and by boiling in alcohol. Crystallinity change was induced by the chemical action of the NaOH treatment.

2. Tenacity was generally decreased by high temperature treatment.

3. The 50-percent span length was affected only very slightly by the atmospheric treatment. The 2.5-percent span length was affected less than the 50-percent span length.

4. The Arealometer fineness value was affected very little by the atmospheric treatment.

5. The high temperature treatment generally resulted in fiber damage as indicated by high ACV.

6. Reduction of surface waxes by boiling in alcohol usually reduced fineness, length and elongation, and increased tenacity.

7. The variability in friction data indicated that the coefficient of friction is dependent upon the normal force.

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THE WIDE-LINE PROTON MAGNETIC RESONANCE SPECTRA OF SOME CELLULOSES

by

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ABSTRACT

Characteristic wide-line proton magnetic resonance absorption spectra of a number of representative cellulose preparations have been obtained in the dry state and after addition of about 7 percent water. Line widths, second moments, spin-spin, and spin-lattice relaxation times have been determined. The second moment of the absorption curve of dry cellulose was found to correlate well with crystalline fraction for most specimens. A technique is described for determining the number of water-cellulose protons exchanging relative to the number of cellulose protons not exchanging. The reduction in absorption line width observed when water is added to cellulose is shown to be quantitatively consistent with such a proton exchange phenomenon.

As part of a continuing investigation of the physical properties of cotton at this Laboratory, the wide-line proton magnetic resonance (NMR) spectra of a number of cellulosic materials of widely differing fine structural characteristics were examined. The observed NMR absorptions reflect the environment and mobility of the nuclei over relatively short distances and in this respect supplement the data of X-ray diffraction and infrared absorption as a measure of molecular order. Relatively few reports dealing with this aspect of cellulose are available and the variation in such parameters as spin-spin relaxation times, line widths, line shapes, and spin saturation behavior and their interrelationships do not seem to have been investigated. Because water has a profound effect on the physical behavior as well as on the NMR spectrum of cellulose, both dry and moist (ca. 7 percent water) samples have been examined. The NMR parameters observed differed significantly in most cases for the range of cellulose types studied and thus provide additional insight for understanding the relationship between cellulose morphology and technological behavior.

EXPERIMENTAL

Samples. — A series of celluloses having a range of supramolecular structural differences were included to establish the variations in NMR spectral characteristics which could be expected in such polymer substrates. They consisted of:

1. Purified (desized, scoured, and bleached) cotton fabric.
2. Mercerized cotton yarn (Lattice types I and II present).
3. Hydrocellulose prepared from purified cotton. The cotton was refluxed with 2.5 N HCl for 1 hour, washed 10 times with distilled water, with a 1 percent NH_4OH wash after the fifth wash, and dried at 80° C. overnight.
4. Hydrocellulose prepared in the same manner as (1) from completely mercerized cotton yarn (Lattice II only present).
5. Fortisan filaments.
6. Textile viscose rayon yarn.
7. Saponified commercial cellulose acetate. The deacetylation was carried out under anhydrous conditions (3), giving a product essentially noncrystalline as judged by X-ray diffraction.
8. Purified cell wall of the marine alga Valonia ventricosa. The purification consisted of refluxing for 5 hours in 1 percent aqueous NaOH, washing, steeping in 0.05N HCl at room temperature for 3 days, washing, and air-drying. The product displayed extremely high lateral order by X-ray diffraction.

A sample of extensively ball-milled cotton cellulose was also examined, but contamination with traces of ferromagnetic material vitiated the data obtained, and results on this specimen are not reported.

NMR measurements. — The NMR measurements were made on approximately 1 gram of sample loosely packed into the bottom of a weighed 15 mm. diameter test tube. After packing in the tube, the samples were dried overnight in an oven at 110° C., the tube was immediately stoppered upon removal from the oven and the dry weight obtained. The wide-line NMR spectrum of the protons was obtained by use of a Varian Model 16B Spectrometer operating at 15 MHz, with a modulation peak-to-peak sweep width of 3.5 gauss. Spectra were recorded from 25 gauss below to 25 gauss above resonance at a sweep rate of 1 gauss/sec. The spectra recorded on an x-y recorder were the usual first derivatives of the NMR absorption signals. Readings of intensity from these curves taken at 1 gauss intervals were used to compute the second moments in gauss^2 and to plot the normalized absorption curve in terms of frequency, using a digital computer. The spin-spin relaxation times were obtained by taking half the peak height of these curves. Line widths (in gauss) were obtained from the first derivative curves between the points of maximum and minimum slope.

After the spectrum of the dry sample was obtained, a micro-syringe was used to inject a quantity of distilled water onto the sample to bring the water-cellulose ratio to about 7 percent on a weight basis. The samples were then sealed and equilibrated overnight to a stable condition. The NMR spectrum was then obtained under the instrumental conditions previously described. Figure 1 represents a typical curve obtained. The conditions under which

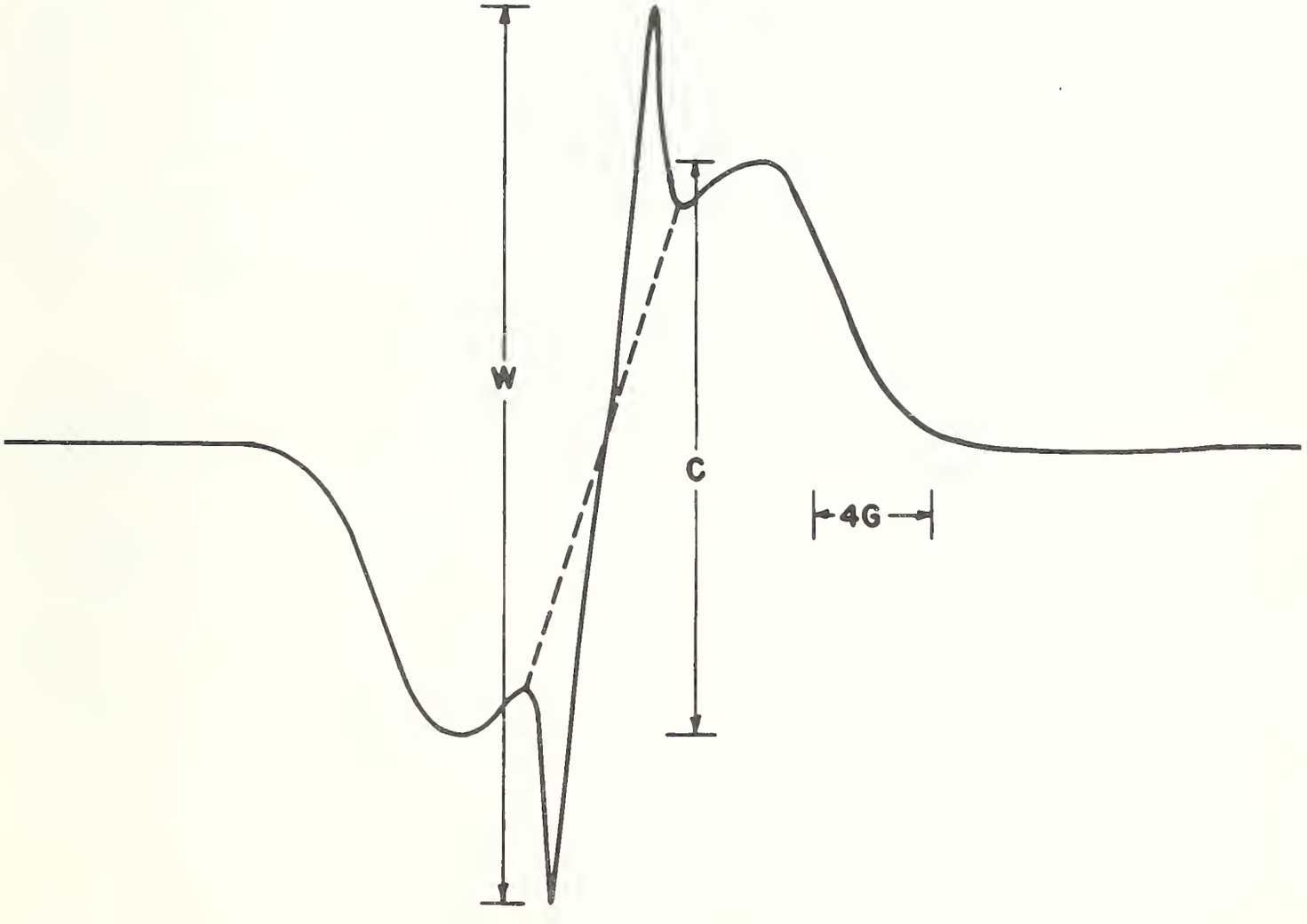

Figure 1. — Typical NMR spectrum for moist cellulose.

these spectra were recorded represent a compromise between those optimum for the wide component (arising primarily from the protons of the cellulose), and those best for observing the narrow component (adsorbed water). As a result, the narrow component has a line width about equal to the modulation sweep width and an intensity diminished because of the high modulation needed to obtain adequate intensity from the wide component of the signal. There is also some loss of intensity due to saturation of the water signal by the radio frequency field. To obtain the line-width of the narrow component of the signal more accurately, samples were run at a modulation sweep width of 0.152 gauss (considerably less than the line widths observed) with a sweep range of 1.0 gauss. In addition, saturation curves were obtained for the narrow component of the signal following the method of Bloembergen, Purcell, and Pound (1). From these saturation curves, comparisons of the spin-lattice relaxation of the water absorbed on the various samples could be made.

DISCUSSION

Dry cellulose. — The parameters obtained from the spectra of the dry celluloses were (1) line-width, ΔH_c (in gauss), (2) the spin-spin relaxation time, T_{2c} (in micro-seconds), and (3) the second moment of the absorption curve about resonance (ΔH_c^2), (in gauss^2). The product $k(= T_{2c}.\Delta H_c)$ was also computed as an indicator of line shape differences, since for similar line shapes this product would be a constant. Table 1 lists the data from these spectra and the X-ray crystallinity data.

The Valonia sample is noteworthy in that in every category except second moment it falls well outside the range of the other samples. The variation in the value of k indicates that there are apparently significant differences in line shape among samples. The line shapes have approximately Gaussian character which has a value of k of about 9×10^{-5} . On the other hand, the small range of the spin-spin relaxation times, T_{2c}, would seem to indicate that the relaxation processes of the protons in the various forms of cellulose are similar.

A plot of the crystalline fraction versus the second moment gave a good straight line fit for all samples except the Valonia and cotton fabric. These are the only specimens of those studied in which the original cellulose crystalline structure is essentially unmodified.

The equation of the best fit straight line for the other six "well-behaved" samples is

Table 1. — Data from spectra of dry celluloses

Sample	ΔH_c gauss	T_{2c} μ sec.	(ΔH^2_c)[1] gauss	k x 10^5	Estimated crystallinity[2] and type
Cotton fabric	11.4	10.5	15.5	11.97	80 pct. -I
Mercerized cotton	12.0	10.3	15.6	12.36	40 pct. -II 10 pct. -I
Hydrocellulose I	10.6	10.5	16.6	11.13	90 pct. -I
Hydrocellulose II	11.6	10.4	16.7	12.06	90 pct. -II
Fortisan	12.4	10.1	16.3	12.52	70 pct. -II
Rayon	12.0	10.6	15.0	12.72	25 pct. -II
Saponified acetate	11.8	10.7	14.4	12.63	0 pct.
Valonia	8.8	11.5	14.7	10.12	100 pct. -I

[1] Corrected for modulation sweep width.

[2] Estimated by method of Patil, Dweltz, and Radhakrishnan (5).

$\overline{(\Delta H_c^2)} = 0.0255X_t + 14.39$, where X_t is the total crystallinity in percent. If one assumes that a cellulosic material consisting of a mixture of lattices I and II plus an amorphous fraction will have a second moment given by $\overline{(\Delta H_c^2)} = X_1 S_1 + X_2 S_2 + X_3 S_3$ where X_1, X_2, and X_3 are the proportions of cellulose I, cellulose II and amorphous cellulose, respectively, and S_1, S_2, and S_3 represent the intrinsic second moments of the corresponding crystal form, then the empirical equation above implies $S_1 = S_2 = 16.94$ and $S_3 = 14.39$ gauss^2. The second moment of an absorption curve which is the sum of two component curves is the weighted average of the second moments of the component curves. This relationship is not true of the line widths and spin-spin relaxation times and thus the failure of these two parameters to correlate with crystallinity as does the second moment is not surprising.

Wet celluloses. — After the addition of water to the dry cellulose samples, two changes were noted. As in previous investigations (2, 9), a narrow component appeared in the spectrum and the wide component experienced a narrowing relative to the dry line width. The peak-to-peak intensities of the narrow component, W, and of the wide component, C, were measured and the narrow component corrected for contribution of the wide component by adjusting the intensities to the background shown (dotted line) in figure 1. The line width of the wide component, ΔH_{cw}, was also obtained, but, in this case, no measurement for the narrow component was made since the wide modulation sweep distorted its line width and indeed the line widths were about equal to the sweep width used. These data, along with the relative water-cellulose concentrations, w/c, are presented in table 2.

The quantity (W/C)/(w/c) shown in table 2 is a comparative measure of the water-cellulose sorption states of the various samples. Several workers (8, 9) have used similar measurements in the investigation of sorption processes. The rather wide range of values observed indicate that although the general process of water sorption on these celluloses may be similar, they are quite different quantitatively and other data verifies these differences.

(W/C)/(w/c) tends to decrease as line width of the wet sample, ΔH_{cw} increases. The line width of the wide component of the moist samples of cellulose showed a decrease from that observed for the dry samples. The differences, $\Delta H_c - \Delta H_{cw}$, ranged from 0.6 gauss for hydrocellulose I to 4.2 gauss for Fortisan.

Table 2. — Data from spectra of wet cellulose

Sample	ΔH_{cw}	W[1]	C[1]	w/c[2]	(W/C)/(w/c)
Cotton fabric	8.4	8.5	7.3	0.061	19.0
Mercerized cotton	10.8	13.2	15.6	.085	10.0
Hydrocellulose I	10.0	13.7	14.6	.066	14.2
Hydrocellulose II	9.0	13.8	12.3	.073	15.3
Fortisan	8.2	14.1	7.2	.073	26.8
Rayon	10.2	12.1	12.2	.066	14.9
Saponified acetate	10.6	5.2	12.4	.063	6.7
Valonia	7.0	11.5	10.2	.069	16.4

[1] In arbitrary units.

[2] Weight of water/weight of cellulose.

At least two explanations have been offered for the narrowing of the wide component of the cellulose signal upon the sorption of water by the sample. One is that it arises from the rapid exchange of protons between the water and cellulose (9); the other, that the water acts as a plasticizer, resulting in freer motion of some of the protons and hence line width reduction.

An attempt was made to analyze the data in such a way as to indicate which of these ideas is correct. It had been noted semiquantitatively that the addition of water to the samples appeared to increase the intensity of the wide component of the signal as well as produce the narrow component. This observation appeared to be consistent with the water-cellulose proton exchange theory, but direct quantitative comparison of spectra was not possible as instrumental and other factors caused the intensities of the spectra obtained in this study to show poor reproducibility. These factors include variation in packing of samples, minor deviations in placement of the sample in the probe and particularly the necessity for periodic retuning of the probe. For these reasons the following technique was devised to provide spectra of the same shape but of intensity appropriate to the protons contributing to the particular spectrum.

The spectrum of the dry sample was placed on the console of a DuPont 310 Curve Resolver and the positive half was matched by an algebraic sum of Gaussian curves. Usually four curves gave an adequate match. The spectrum of the dry sample was now replaced on the console of the instrument by that of the wet sample. The base line and resonance point of the dry sample curve image, stored on the oscilloscope, and that of the wet sample curve were then put in coincidence. The intensity of the dry sample curve image was not adjusted to the maximum value which would fit within the wet sample curve. A second set of Gaussians were now added algebraically to the first set to provide a match of the positive half of the wet sample curve. About three additional curves were required to make this match in most cases. The curves generated by these two sets of curves and their sum were now recorded on an X-Y recorder (fig 2) slaved to the curve resolver and the area under each set of curves determined from the meter on the instrument provided for this purpose. The curve marked c represents protons of cellulose not interacting with water, i the protons of water and cellulose which are exchanging and that marked cw the spectrum of the wet sample, which is the sum of the other two.

By setting the curve c, which still has line width ΔH_c, to the maximum value that could be included under the curve cw representing the spectrum of the wet sample, it thus represents the maximum number of protons of cellulose not interacting with the water that can be tolerated by the wet sample spectrum intensity. This quantity is denoted as $\hat{p}_c$. Similarly, curve i, represents the quantity of water and cellulose protons interacting, p_i. The protons in the narrow component are neglected. The following technique was used to obtain values of p_i. The area under the first half of the derivative curve is given by

$$A = \int_{-\infty}^{0} g'(v)dv = 2T_2 = k/\Delta H \qquad (1)$$

where k is a constant depending on the line shape g(v) and v is the deviation of the frequency from resonance (in Hz). The peak-to-peak height, h, of derivative curve is proportional to T_2^2 and hence to $(k/\Delta H)^2$. The spectra associated with any one sample are assumed to have similar line shapes; that is, k is a constant for all spectra associated with a particular sample. Letting A, with the appropriate subscript, represent the area under the curve represented in figure 2 and h (subscripted) the height of the corresponding curve, one obtains the following relationships:

$$\frac{p_i}{\hat{p}_c} = \frac{A_i \Delta H_i}{\hat{A}_c \Delta H_c} \qquad (2)$$

$$\frac{p_i}{\hat{p}_c} = \frac{h_i}{\hat{h}_c}\left(\frac{\Delta H_i}{\Delta H_c}\right)^2 \qquad (3)$$

In principle the line width ΔH_i could be measured directly from the curve generated by

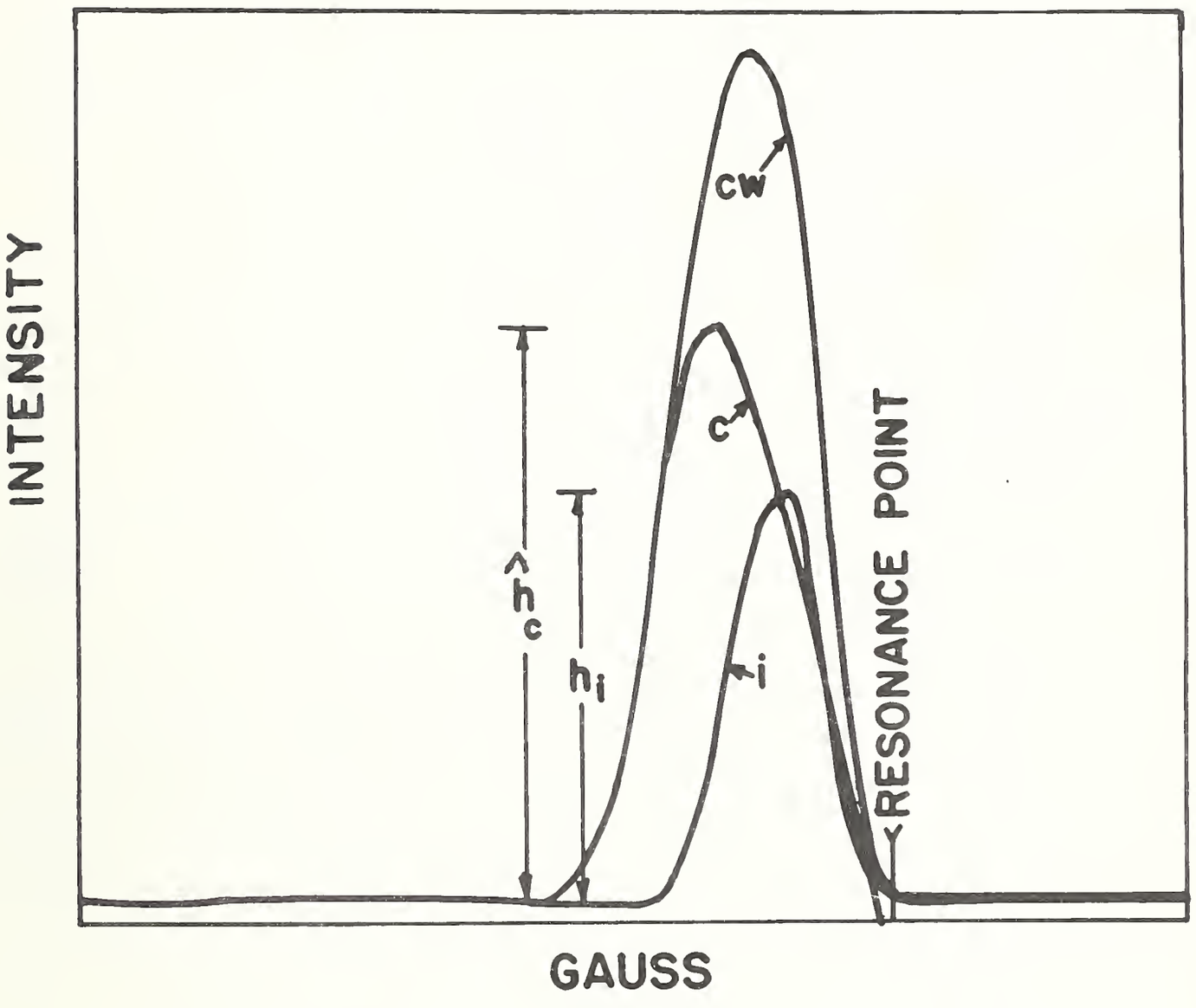

Figure 2. — Curves obtained from curve analyzer. Curve cw represents positive half of signal obtained from moist cellulose (neglecting narrow component). Curve c represents signal from dry cellulose adjusted to maximum intensity that can be included under curve cw.

Curve i is the difference between curves cw and c represents the part of curve cw arising from exchanging water and cellulose protons.

the curve analyzer. However, because of the uncertainties in precisely locating the peaks, the values were obtained from the solution of equations 2 and 3:

$$\Delta H_i = (A_i/\hat{A}_c)(\hat{h}_c/h_i)\Delta H_c, \qquad (4)$$

and are reported here. Since $p_i + \hat{p}_c = 1$, one may use this fact and the values of ΔH_i obtained from Eq. (4) to calculate the values of p_i and $\hat{p}_c$. These values are shown in table 3 along with those of ΔH_i. To determine the consistency of our procedure, we now combined graphically two gaussian curves, with the aid of a digital computer, with widths ΔH_i ΔH_c and weighted p_i and $\hat{p}_c$, respectively, to give a calculated value of ΔH_{cw} as measured from the computer plot. The calculated and observed values are presented in table 3. The agreement is reasonable and supports the theory that the line narrowing observed when moisture is added to cellulose is indeed due to exchange between some of the water and cellulose protons.

Table 3. — Calculated proton counts and line widths

Sample	P_i	P_c	ΔH_i	ΔH_{cw}	
				Calculated	Observed
Cotton fabric	0.194	0.806	7.25	9.3	8.4
Mercerized cotton	.086	.914	7.74	10.9	10.8
Hydrocellulose I	.194	.806	7.42	9.3	10.0
Hydrocellulose II	.181	.819	8.13	10.2	9.0
Fortisan	.227	.773	7.92	9.9	8.2
Rayon	.153	.847	7.80	10.3	10.2
Saponified acetate	.276	.724	9.77	10.9	10.9
Valonia	.158	.842	4.66	6.2	7.0

The hypothesis that the protons, p_i, consisted of equal numbers of cellulose protons and water protons exchanging was tested. For four of the samples, this required water protons in excess of the added amount be present. Thus, it may be concluded that, in general, more cellulose protons than water protons were involved in the exchange.

Narrow component of the spectra. — The narrow component of the spectra of water-cellulose systems has received more attention as a means of measuring sorbed water quantitatively (4, 6, 7, 10) and for gaining a fuller understanding of the sorption processes. Several workers have reported evidence for the existence of protons in this region of the spectra with several spin-spin and spin-lattice relaxation times. The variation in spin-spin relaxation times is observed by changes in line widths with change in water content, while pulsed RF techniques seem to be most useful in the determination of multiple spin-lattice relaxation times.

The line widths, ΔH_W, were determined by the method previously mentioned and the spin-spin relaxation times calculated from the Gaussian relationship $T_{2W} = 0.37 \times 10^{-5}/\Delta H_W$. These data along with the relative spin-lattice relaxation times determined by the progressive saturation method of Bloembergen and others (1), using a gadolinium chloride solution as a standard, are presented in table 4. These data indicate a general increase of the spin-spin relaxation time, T_{2W}, with an increase of the quantity (W/C)/(w/c). (W/C)/(w/c) is thus generally related to both T_{2W} and ΔH_{CW} among these samples, which relates the intensity of the narrow to the broad component of the spectra. This is an indication of the sensitivity of (W/C)/(w/c) as a comparative measure of the sorption mechanisms and their associated relaxation processes.

Figure 3 shows a typical plot of a progressive saturation curve for hydrocellulose I. The anomalous behavior of the saturation curve at

Table 4. — Parameters of narrow component of spectra

Sample	ΔH_W gauss	T_{2W} millisec.	T_{1W} millisec.
Cotton fabric	0.23	0.408	11.0
Mercerized cotton	.30	.312	4.9
Hydrocellulose I	.24	.390	9.8
Hydrocellulose II	.23	.408	6.1
Fortisan	.19	.594	7.8
Rayon	.30	.312	2.5
Saponified acetate	.37	.254	2.4
Valonia	.17	.552	6.2

points indicated by arrows is probably due to the existence of multiple spin lattice-relaxation times and for this reason the relaxation times reported here should be regarded as approximate. The following relationship was used to calculate the relative spin-lattice relaxation time between the sample, A, and the standard, B,

$$\frac{T_{1A}}{T_{1B}} = \frac{H_B}{H_A} \frac{\Delta H_{wA}}{\Delta H_{wB}} \qquad (5)$$

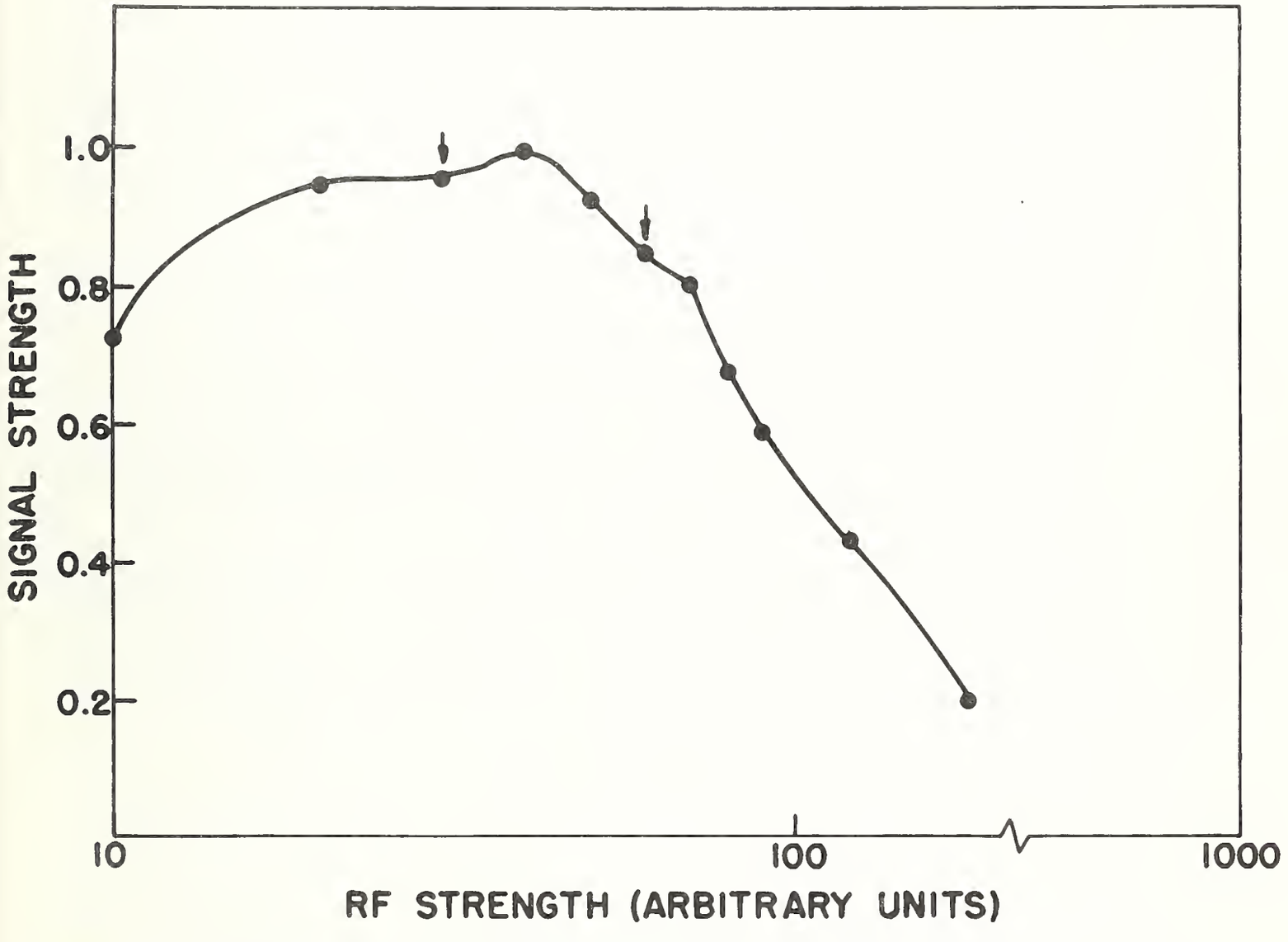

Figure 3. — Typical progressive saturation curve (Hydrocellulose I). Arrows indicate points anomalous behavior suggesting the existence of other spin-lattice relaxation times.

where T_1 is the spin-lattice relaxation time, H the RF field strength at half maximum signal, as shown in figure 3, and ΔH_W the line width of the water signal given in table 4.

CONCLUSIONS

Wide-line NMR spectra of dry cellulose have been shown to be related to the crystalline fraction in a number of samples covering a wide range of supramolecular morphologies. In particular, the second moments of the absorption curves are linearly related to the percent crystallinity as determined by x-ray diffraction, Valonia and cotton being exceptions. It is concluded that the "intrinsic" second moments of spectra of cellulose I and cellulose II are the same and differ from that of amorphous cellulose. The failure of the line widths and spin-spin relaxation times to follow a linear relationship with crystallinity is consistent with the hypothesis that the sorption curves are the sum of two or more component curves.

A technique has been developed which enables a measurement of the number of water protons and cellulose protons exchanging relative to the number of cellulose protons not exchanging with water. The parameters developed by this technique are in fair agreement with the experimental data on line narrowing of the cellulose spectra upon the addition of water at the concentration levels examined here.

The quantity (W/C)/(w/c), the ratio of the peak-to-peak intensities of the narrow to wide component with respect to water concentration, has been shown to be related to the spin-spin relaxation time of the narrow component, $T_{2\,W}$, and the line width ΔH_{CW}, of the broad component of the wet sample. Its use as a comparative index of the water sorption processes on cellulose is suggested.

The general picture of the water-cellulose sorption system obtained from this and previous studies of others suggests the existence of protons in the system in five environments or states, including:

1. Protons in the crystalline part of the cellulose, characterized by a second moment of about 17 gauss^2 .

2. Protons in the amorphous regions of the cellulose characterized by a second moment of about 14 gauss^2 .

3. Protons of water and cellulose which exchange rapidly, resulting in a signal deduced to have line widths ranging from about 5 gauss to about 10 gauss.

4. Protons of water primarily responsible for the narrow component of the observed spectrum and having spin-lattice relaxation times ranging from about 2.5 to 11 milliseconds.

5. Protons of water with spin-lattice relaxation times shorter than those in state 4, as evidenced by anomalies in the saturation curves in this study and measured separately by others (6), which represent more tightly bound water.

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CONVOLUTION ANGLE AND ITS EFFECT ON ORIENTATION MEASUREMENTS

by

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The mature cotton fiber is a flat hollow tube which twists to varying degrees along its length, thus giving rise to the existence of convolutions. Figure 1 shows a scanning electron microscope picture of convolution. These form after the boll opens and the protoplasm within the lumen begins to dry. There is no single explanation for their cause but it has been suggested that the underlying spirality of the fibrillar elements of the secondary wall gives rise to their formation (1). Whatever their cause, it is generally agreed that the presence of the convolutions greatly affects many of the physical properties of the cotton fiber.

Betrabet (2,3) has shown that the tensile strength of 22 varieties of cotton can be correlated with a convolution angle which was measured optically. Figure 2 illustrates the technique involved in the measurement of this angle. The parameters involved can be easily measured with the aid of a low power microscope and an eyepiece grating. In this investigation 300 determinations were made, for each of 10 varieties studied. In table 1 average values of convolution angle for each variety are given along with the birefringence, the 50 percent intensity X-ray angle and the spiral angle. The birefringence noted in each case is the difference between the refractive indices taken parallel and perpendicular to the fiber axis using the well known Becke line method of measuring refractive index. Approximately 50 determinations were made in each direction.

The X-ray angle is the angle at which the intensity of the azimuthal scan of the 002 plane becomes 50 percent of the total scattered intensity (4). The values reported in this table are averages of those from duplicate fiber bundles weighing approximately 35 milligrams each. The values are within $\pm 1.0^{\circ}$.

The spiral angles were measured according to a theoretical technique described by Hartshorne in Nature, 1959 (5). His theory stated that, due to the spiral structure, the top and bottom walls of a flat, ribbon-like cotton fiber in a polarizing microscope, would behave optically in a manner similar to two superimposed transparent crystalline plates oriented to one another by an angle equal to twice the spiral angle. By appropriate manipulation of the analyzer and microscope stage, the angle between the vibration direction of light coming from the top plate and the component passing the analyzer at extinction can be measured experimentally. This angle is proportional to the spiral angle according to a simple trigonometric expression. This technique can only apply completely for one particular wavelength, but, according to Hartshorne, a close approximation can be realized by working in the center of the visible spectrum. The work reported here was carried out with the green line (546 millicrons) of a mercury vapor lamp, isolated by an appropriate filter and a microscope equipped with polarizing optics and a rotating stage. Approximately 50 determinations were made for each variety.

The mean value of the spiral angle for all varieties combined was 21.7°. Application of a statistical test of variance between all varieties and this mean value indicated that, at the 99.5-percent level of confidence, the differences were insignificant (6). It should be pointed out that these measurements were taken between convolutions or where the fiber closely approximates a flat ribbonlike structure.

In figure 3 we see the relation between convolution angle and X-ray angle. The coefficient of correlation is significant at the 99 percent level of confidence. It is interesting to note that the slope of the regression equation

Figure 1. — Electron microscope picture of a convolution.

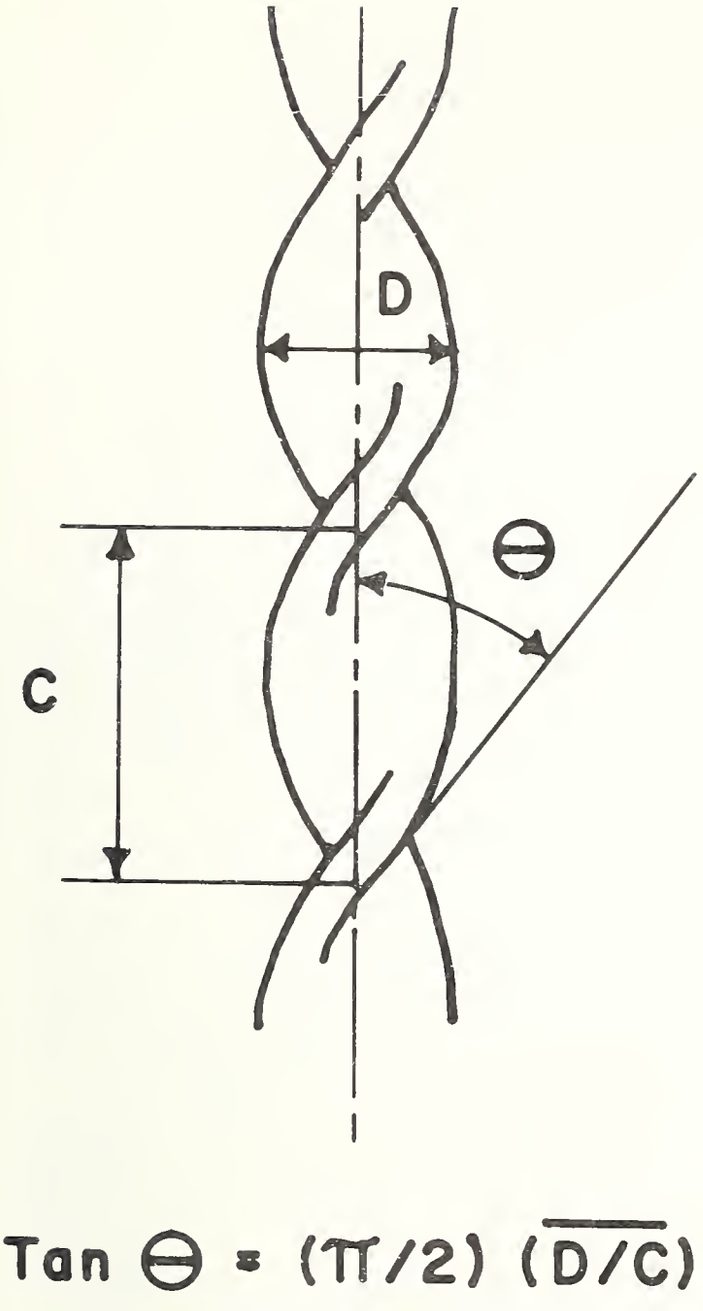

Figure 2. — Technique for measuring convolution angle.

approaches unity and also that the intercept, i.e., X-ray angle at "O" convolution angle closely approaches the value of the optically measured spiral angle.

Figure 4 illustrates the relation between birefringence and convolution angle. Again the correlation is good. We shall return to this relation later.

To evaluate the effect of convolutions birefringence data, the birefringence of a perfectly oriented, unconvoluted fiber must be known. Figure 5 illustrates the relationship between the birefringence and X-ray angles for the 10 varieties of cotton studied along with an additional specimen, ramie. It is well known that ramie is a highly oriented fiber, hence the high birefringence value and low X-ray angle. From these data we can denote ΔN_O as the birefringence of a fiber having perfect fibrillar orientation, that is, an X-ray angle of essentially zero degrees. This value is taken as the intercept of the regression equation or 0.071 which agrees with the values in the literature.

If now we return to the previous relation, that is, the birefringence-convolution graph (figure 4) and carry out the same reasoning, the result is the birefringence of a cotton fiber which is unconvoluted, though not necessarily perfectly oriented. This value we find is 0.057.

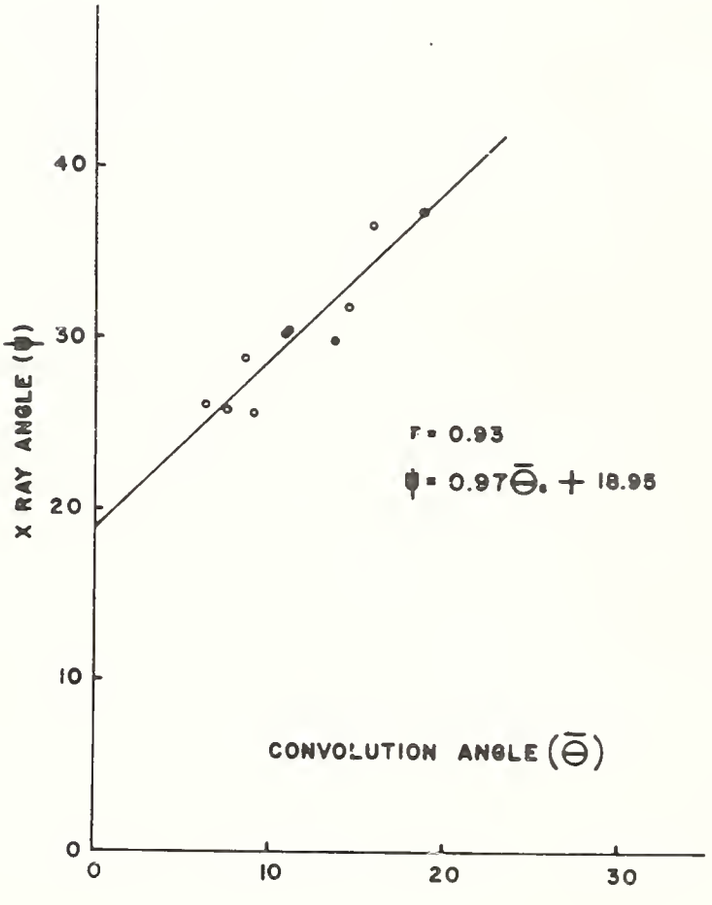

Figure 3. — The relationship of X-ray angle to convolution angle for ten cotton varieties.

Table 1. — Orientation measurements of selected cottons.

Variety	Spiral angle	X-ray angle	Convolution angle	Birefringence
	Degrees	Degrees	Degrees	
Mysore American	22.15	37.3	13.6	0.044
Devity	21.85	36.5	11.5	.042
Bobshaw	21.68	31.8	10.5	.045
Laxmi	21.45	30.4	8.0	.049
Pima S-1	21.40	30.1	7.8	.052
Stoneville 2B	21.91	29.7	9.9	.049
Gaorani 12	21.70	28.8	6.2	.051
Del Cerro	21.79	25.7	5.4	.050
"G. arboreum"	21.38	26.0	4.5	.053
St. V. Sea Island	21.43	25.5	6.5	.048

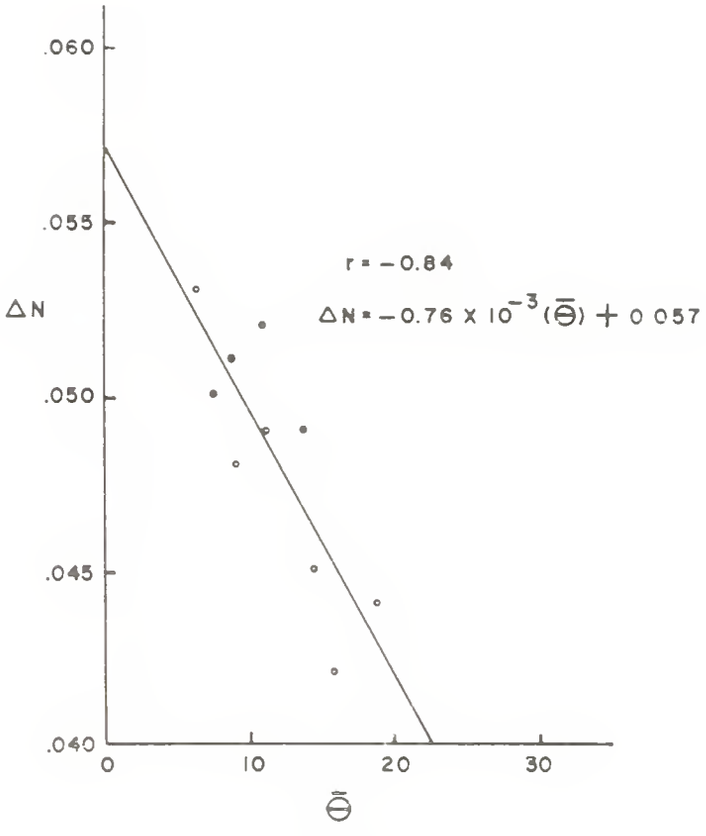

Figure 4. — The relationship of birefringence to convolution angle for ten cotton varieties.

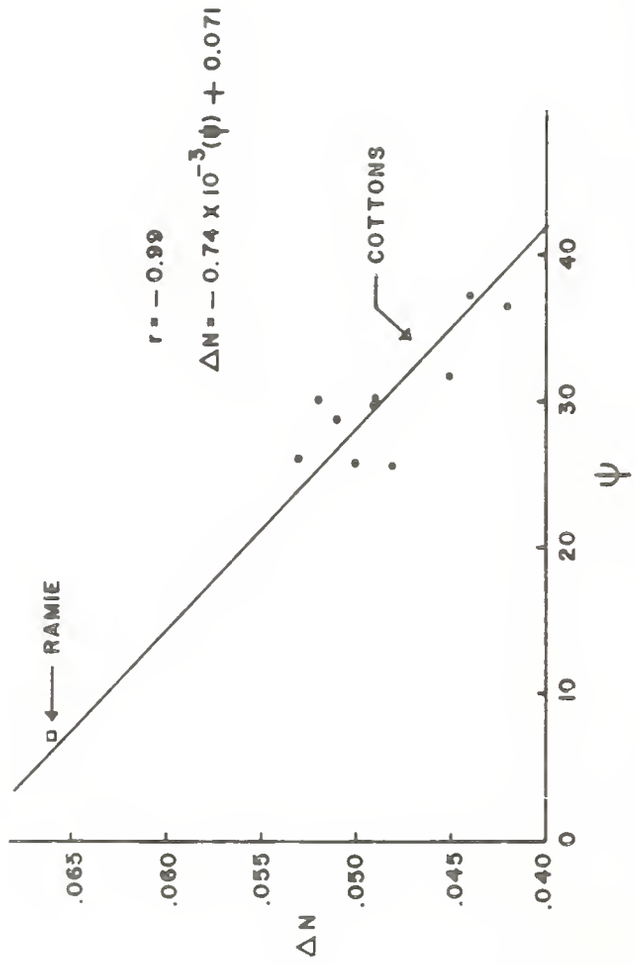

Figure 5. — The relationship of birefringence to X-ray angle for ten cotton varieties and ramie.

To relate these values to spiral or angular orientation within the cotton fiber, use is made of Hermans' optical orientation factor (7) (figure 6). Substituting the previously determined values and solving for gamma, we find gamma equal to 21.25°, which is very close to the 21.7° found according to the Hartshorne technique.

$$\frac{\Delta N}{\Delta N'} = 1 - \sin^2 \gamma$$

Where $\Delta N'$ = birefringence at 0 x-ray angle (Ψ)
ΔN = birefringence at 0 convolution angle (Φ_c)

Figure 6. — Herman's optical orientation factor.

Many of the physical properties of fibers are directly affected by the orientation of the subfiber elements. It is for this reason that the X-ray angle is considered an important measurement and is often correlated with such properties as strength, elongation, and modulus. In figure 7 we see the relationship between X-ray angle and tenacity. The tenacity was measured at a zero nominal gage length using the Stelometer and the samples were all conditioned for 24 hours at standard conditions before testing. Figure 8 shows the same tenacity values correlated now to the convolution angles. It is interesting to note the similarity between the slope of this regression line and that of the previous slide. The correlation coefficients are also similar.

In conclusion, our data indicate that X-ray measurements of fibrillar orientation using fiber bundles are distorted by the presence of convolutions within the individual fibers and the extent of convolution formation within a fiber if reflected in birefringence measurements.

Furthermore, the data presented here are believed to strengthen the hypothesis advanced by Meredith (8) that the spiral angle in an unconvoluted fiber may be a constant independent of genetic variety.

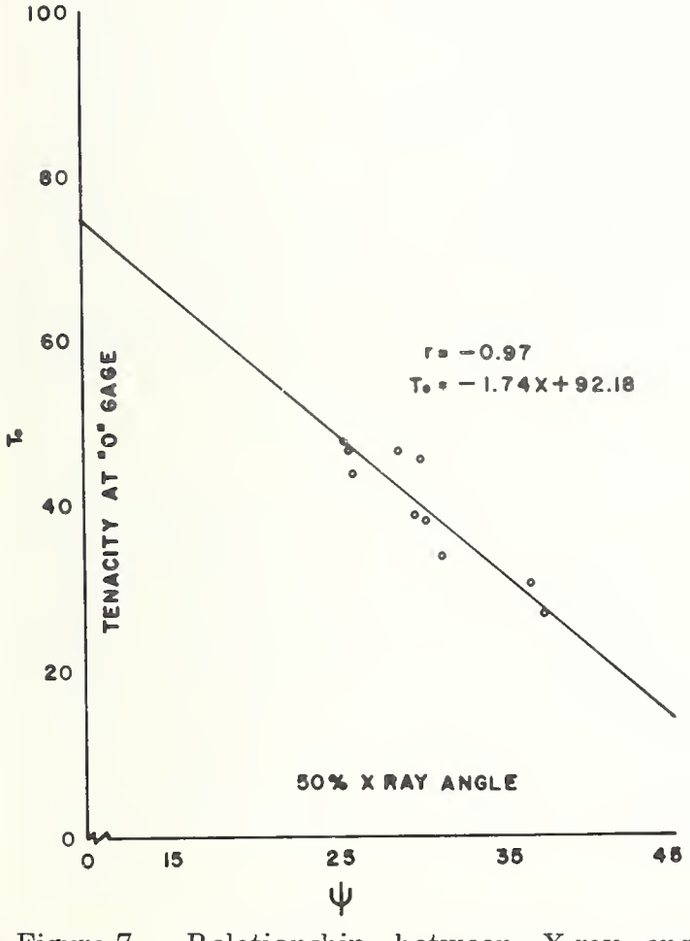

Figure 7. — Relationship between X-ray angle and tenacity

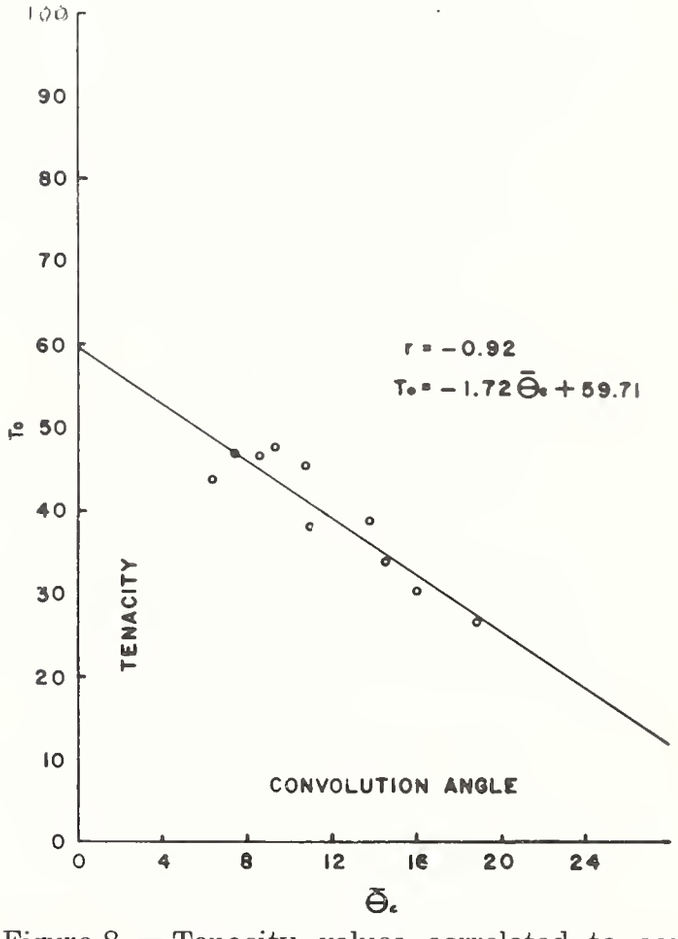

Figure 8. — Tenacity values correlated to convolution angles.

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RECOVERY OF SINGLE COTTON FIBERS TAKEN FROM FORMALDEHYDE CROSSLINKED YARNS

by

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(Presented by Louis C. Weiss)

ABSTRACT

Single fibers of Deltapine cotton were taken from low twist yarns that had been ethanol extracted and crosslinked under slack condition by conventional, dry-cure formaldehyde and different aqueous formaldehyde solutions. Single cotton fibers lose breaking loads and elongations with increasing crosslinks. Crosslinks introduced in swollen fibers cause less loss than those introduced in nonswollen fibers. Tensile strain recovery of single fibers increases with increasing crosslinks. The increase in tensile strain recovery is directly related to the increase in tensile energy recovery if both are measured under the same conditions. Individual cotton fibers increase in tensile recovery and compliance when crosslinked in a slack yarn. Single cotton fibers retain strength and increase recovery, as displayed by fibers crosslinked in a aqueous formaldehyde solution containing sulfuric acid.

INTRODUCTION

As part of the continuing program to improve the performance of durably pressed cottons, it becomes necessary at times to investigate the individual fiber. Are the changes in mechanical properties of the single cotton fiber the same for slightly different chemical treatments? Are the changes produced in a modified yarn or fabric caused by the changes in the mechanical properties of the fiber or to the interaction of fiber on fiber? As crosslinked cottons are required to be serviceable under various environmental conditions, what are the properties of single fibers under conditions other than dry?

The following report is an aid in answering such questions for crosslinking treatments. The recoveries from various strains and the breaking strengths of differently modified single cotton fibers are presented for two separated conditions.

SAMPLES

A Deltapine cotton was processed into a 14/3 yarn with the low twist multiplier of 3. This greige yarn was ethanol-extracted and received various chemical treatments. All treatments and each step of a treatment were carried out with the yarns in a slack condition. Details of the treatments have been published (2) and the different classes are tabulated below:

TREATED COTTON SAMPLES

1. Control, ethanol extracted.
2. Form C, conventional dry-cure.
   A series of aqueous solutions with three different concentrations of formaldehyde (HCHO) - 4, 10, and 20 percent – and zinc nitrate as catalyst.
3. Form D, 4 percent formaldehyde in 18 percent water with acetic acid.
4. Form W, 8 percent formaldehyde in 75 percent water with hydrogen chloride.
5. Form S, 8 percent formaldehyde in 18 percent water and 47 percent sulfuric acid with acetic acid.

STRENGTH

Single fibers were removed from the yarns, combed, and relaxed before testing. The mechanical measurements were made on an Instron Tester equipped with an automatic

integrator and environmental chamber. A pretension of 0.1 gm. was applied to each fiber. The rate of loading was such that the time required for a direct break would be approximately 40 seconds. The direct, noncyclic load- elongation curve and the energy-to-break were determined. The average breaking-point valves were obtained from 100 specimens. One-quarter of an inch was the nominal gage length with 10 percent of the specimens from each sample measured to obtain the average gage length of that sample. Each sample was evaluated under a relative humidity of 65 percent and soaking wet conditions, both, at a temperature of 70°F. Standard test conditions for cotton, 70°F., 65 percent R.H., are sometimes called "Dry" or "Conditioned" in the wash-wear trade.

Bound formaldehyde was determined by the digestion-distillation method (6) and used as an index of the extent of chemical treatment. Unfortunately, there is a progressive loss in strength of the single cotton fiber for increasing bound formaldehyde. Figure 1 shows this for the series of Form C fibers measured under wet and standard conditions. The difference between fiber strengths under the wet vs. standard conditions of test is considered not significant. This series terminates at an estimated 10 crosslinks per hundred anhydroglucose units. This is equivalent to the great number of crosslinks currently being used in the durable-press industry.

The mean values from direct breaks, characterizing every sample under standard and wet

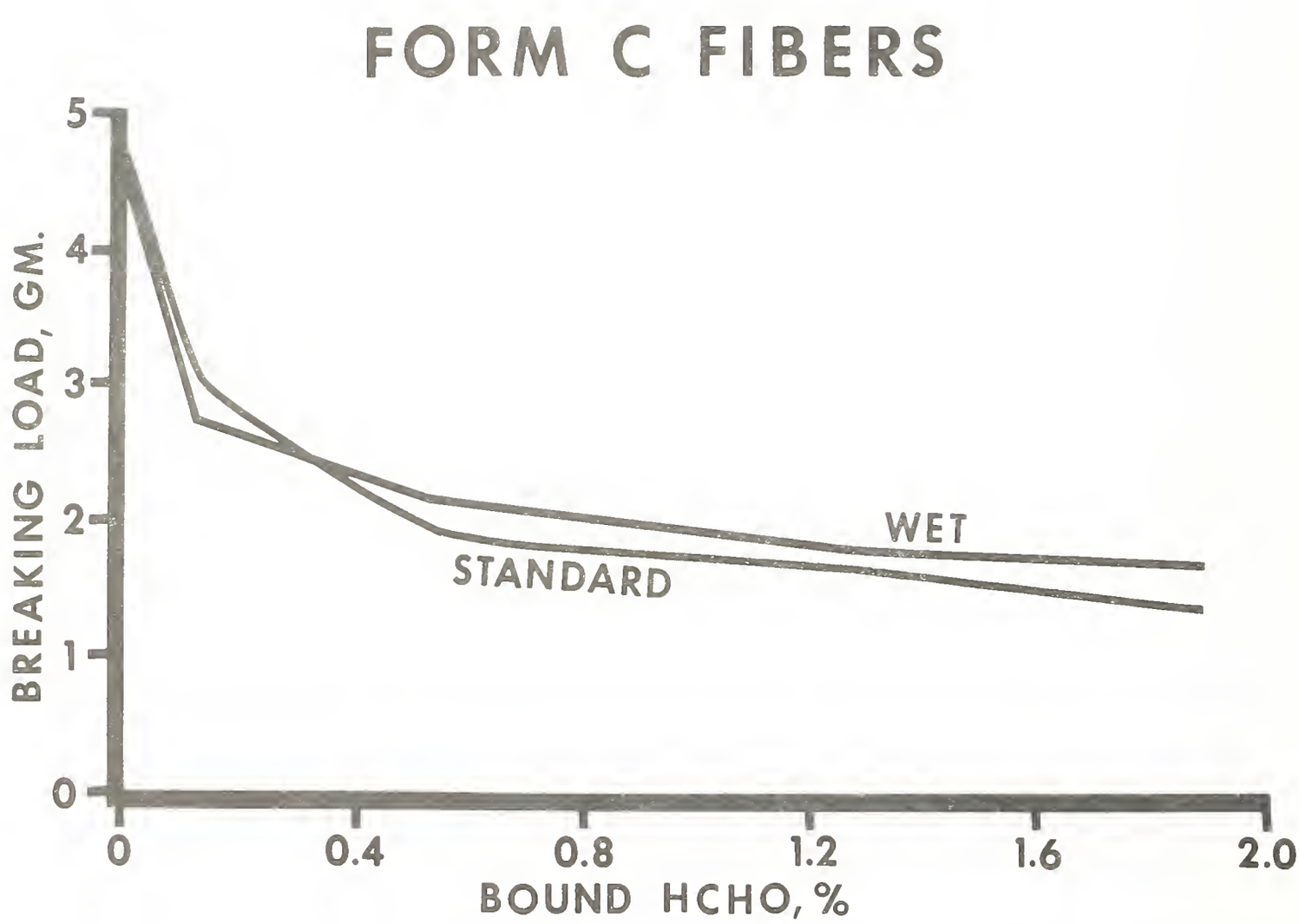

Figure 1. — Losses in strength for single cotton fibers with respect to bound formaldehyde for the dry-cure, conventional, formaldehyde treatments—measured under wet and standard conditions.

Table 1. — Tensile strength and chemical reaction for single cotton fibers

Treatment	Standard		Wet		Bound HCHO
	Load	Elongation	Load	Elongation	
	G.	Pct.	G.	Pct.	Pct.
Extracted	4.7	9.6	4.7	10.6	0.0
Form C	3.0	6.9	2.8	6.6	.11
Form C	1.9	4.2	2.2	5.2	.52
Form C	1.4	2.9	1.7	4.1	1.88
Form D	2.2	5.3	1.9	5.4	.43
Form W	1.8	5.3	1.7	6.2	.46
Form S	3.3	7.6	4.1	8.4	.91

conditions, are listed under tensile strength in table 1. A decrease in breaking load and elongation resulted from all formaldehyde crosslinkages.

A scant modulus indicating fiber stiffness can be calculated for each sample in table 1 by dividing its breaking load by percent elongation. The moduli of these single cotton fibers show a decrease rather than an increase in stiffness over the control. Where treated in a slack yarn, the tensile moduli of single cotton fibers are reduced by crosslinking. This extends to formaldehyde crosslinkages the results published by Rebenfeld for nitrogeneous resins (5).

Where single fibers from these samples are tested under wet conditions, the breaking points of the conventionally crosslinked fibers are near a straight-line corresponding with the modulus of the control. Again, the decrease in tensile stiffness for wet fibers is consistent with the decrease for conditioned fibers.

Cellulose crosslinked by formaldehyde under sulfuric acid-water swollen conditions is an exception from other crosslinked samples. Under wet conditions, cotton fibers from this sample have an average stiffness significantly higher than their controls. This modified cotton also is reported to have an unusual, preferential location of crosslinks near the periphery of the fiber (1). Conceivably this crosslinked region could act as a lateral, cylinderical tube supporting the water swollen, internal fiber components. Such a composite structure, analogous to a metal tube filled with sand, could produce the observed unusually high rigidity. The fibers of Form S also retain unusually high breaking loads and elongations for crosslinked cellulose. This results in a relatively high toughness for Form S fibers under both standard and wet conditions.

Other comparisons indicate the extent of the modifications for formaldehyde crosslinked, single cotton fibers. The changes in tensile modulus due to crosslinking is less than the differences that exist among various varieties of native cottons (8). But to reduce the breaking load and elongation equal to that due to the higher bound formaldehyde of Form C, crosslinking would require extensive thermal (4) degradation of the native, single cotton fibers.

STRAIN RECOVERY

Figure 2 approached an idealized deformation for a single cotton fiber and its recovery from fiber strain. Recoverable deformation was measured from several locations along the load-elongation curve after allowing a relaxation time of 3 minutes (3). This measured recoverable deformation was then calculated as a percent of the applied strain to give tensile strain recovery for single cotton fibers.

Thirty specimen per sample were measured to obtain the tensile recovery values. The mean tensile strain recoveries are summarized in table 2 from formaldehyde treated single cotton fibers. Tensile recoveries from each of two different strains, 0.02 and 0.03, are tabulated under the two different moisture conditions. For these individual fibers, there is an appreciable difference between percentages from the

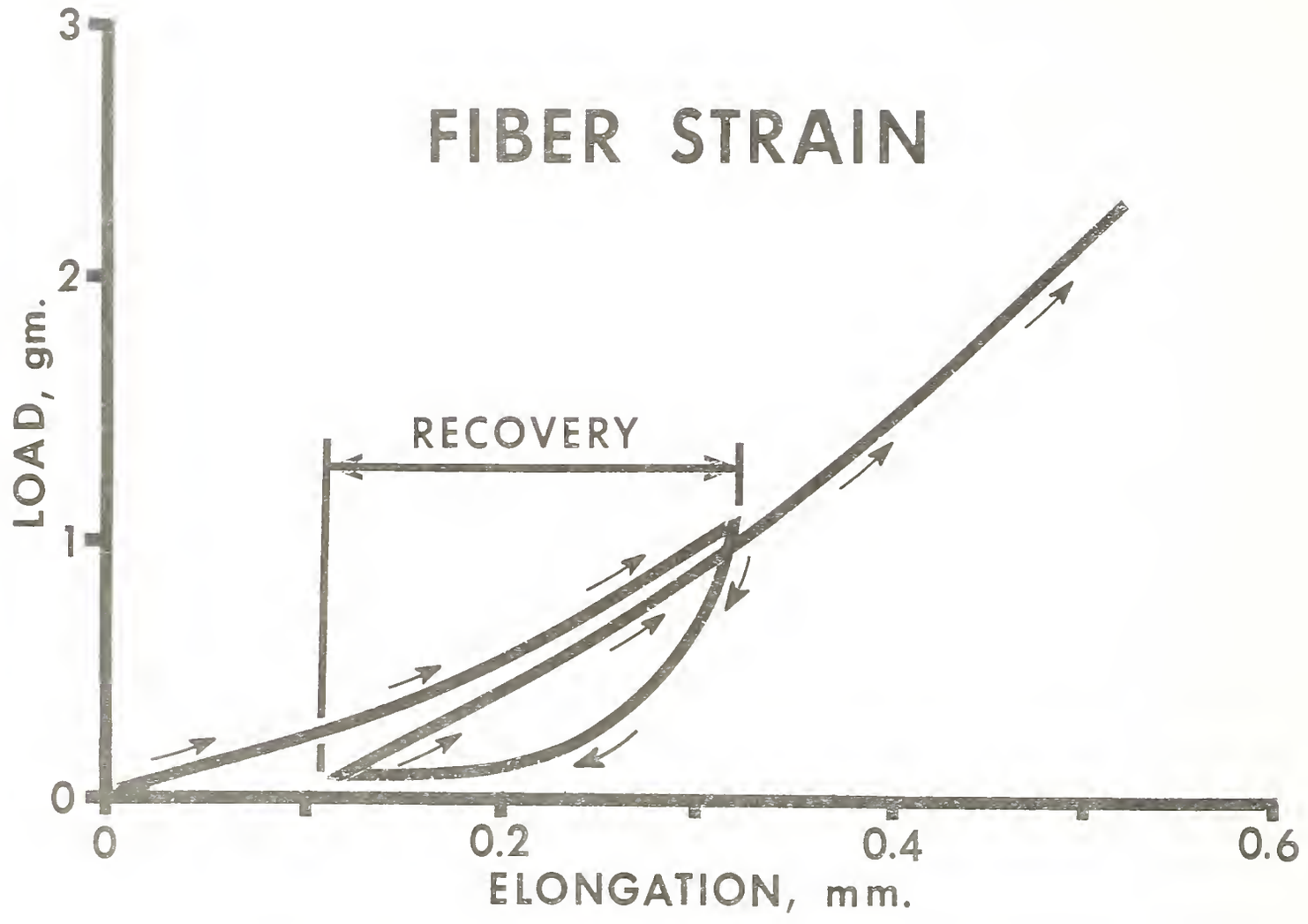

Figure. 2. — Tensile strain recovery for a single cotton fiber.

extracted control and from the high level of dry-cure treatment. Increasing the strain from which recovery is measured decreases the percentage of tensile recovery. This is illustrated by the recoveries from strains of 0.02 as compared with those from 0.03. Increasing chemical reaction while using the same treatment increases tensile recovery as illustrated by the recoveries within the conventional formaldehyde group. For the formaldehyde dry-cure treatment, the recovery of single fibers under standard conditions is equal to or higher than their recovery when wet.

DIFFERENTIAL RECOVERY

For comparing chemically treated cottons under different environmental parameters, perhaps more informative than the recovery value is the difference in recovery between the modified sample and the extracted control where both are measured under the same humidity and from the same strain. This change in recovery can then be normalized as a percent of the recovery of the control and designated as differential tensile strain recovery (7). By definition, Differential

Table 2. — Percentage of tensile strain recovery for single fibers

Treatment	Strain				Bound HCHO
	Standard		Wet		
	0.02	0.03	0.02	0.03	
	Pct.	Pct.	Pct.	Pct.	Pct.
Extracted	83	73	68	54	0.0
Form C	84	73	73	64	.11
Form C	88	84	84	80	.52
Form C	92	87	87	83	1.88
Form D	84	78	84	78	.43
Form W	86	82	84	76	.46
Form S	87	79	90	90	.91

Strain Recovery, percent is the Recoveries of, $\left[\frac{\text{Treated-Extracted}}{\text{Extracted}}\right]100$.

In table 3 the differential tensile strain recovery for the formaldehyde crosslinked fibers, determined from 0.02 strain under standard conditions of 70°F. and 65 percent R.H., is compared with the chemical reaction expressed as bound formaldehyde. For these modified cottons, the differential strain recovery is always an increase or improvement over the control and increases with increasing bound formaldehyde.

Table 3. — Differential tensile strain recovery in percentage from 0.02 strain

Treatment	Standard	Wet	Bound HCHO
	Pct.	Pct.	Pct.
Extracted	0	0	0.0
Form C	1	7	.11
Form C	6	23	.52
Form C	11	28	1.88
Form D	1	23	.43
Form W	4	24	.46
Form S	5	32	.91

At equivalent crosslinks and standard conditions conventional formaldehyde fibers modified while collapsed have greater recovery than any of the other formaldehyde fibers--all of which have been modified while swollen to some extent.

Table 3 also presents the differential tensile strain recovery of fibers tested when soaking wet. The increase in recovery due to the initial crosslinking is greater under the wet than under the standard test conditions. At the same level of crosslinking, the improvement in recovery caused by crosslinks introduced under the water swollen conditions (Form W) are now equal to or greater than those caused by crosslinks introduced under the dry, collapsed fiber conditions (Form C). The positions of the cottons crosslinked with formaldehyde while swollen in water are reversed relative to cottons crosslinked while collapsed. This reversal in ranking illustrates that single fibers show larger increases in recovery when measured under a moisture approximating their condition during crosslinking.

The increase in recovery for crosslinked single cotton fibers determined under wet conditions is higher than their increase under standard conditions. The differences between recoveries determined under wet and standard conditions appear greater for single fibers than the recoveries reported for the yarns from which these fibers were taken (2, 7).

RECOVERIES OF STRAIN AND ENERGY

The tensile recoveries of strain and energy for the single cotton fibers are measured, under standard conditions and by wet test, from the deformation due to a 1 gram load. As before, the difference between the modified sample and its control are calculated as a percent of the control. These differential tensile recoveries indicate an increase or improvement in the recoveries of strain and energy for all samples.

Increased tensile strain recovery as related to increased tensile energy recovery is presented in figure 3. The recoveries separate according to

atmospheric conditions of testing. The linear relation between these recoveries measured under standard conditions has a correlation coefficient of 0.97. Comparable calculations for recoveries under wet test give a correlation of 0.79. The differential tensile energy recoveries are greater under standard than under wet conditions.

Crosslinked single cotton fibers fail to display the one-to-one correspondence for tensile recoveries of strain and energy when measured under, both, standard and wet conditions of test. Where the humidity is specified, an interchange of information between energy recovery and strain recovery is possible for single cotton fibers.

SUMMARY

Tensile properties for extracted cottons and cottons crosslinked with formaldehyde are presented for single fibers under wet as well as standard test conditions. Under each condition, crosslinked single cotton fibers lose breaking load and elongation with increasing crosslinks.

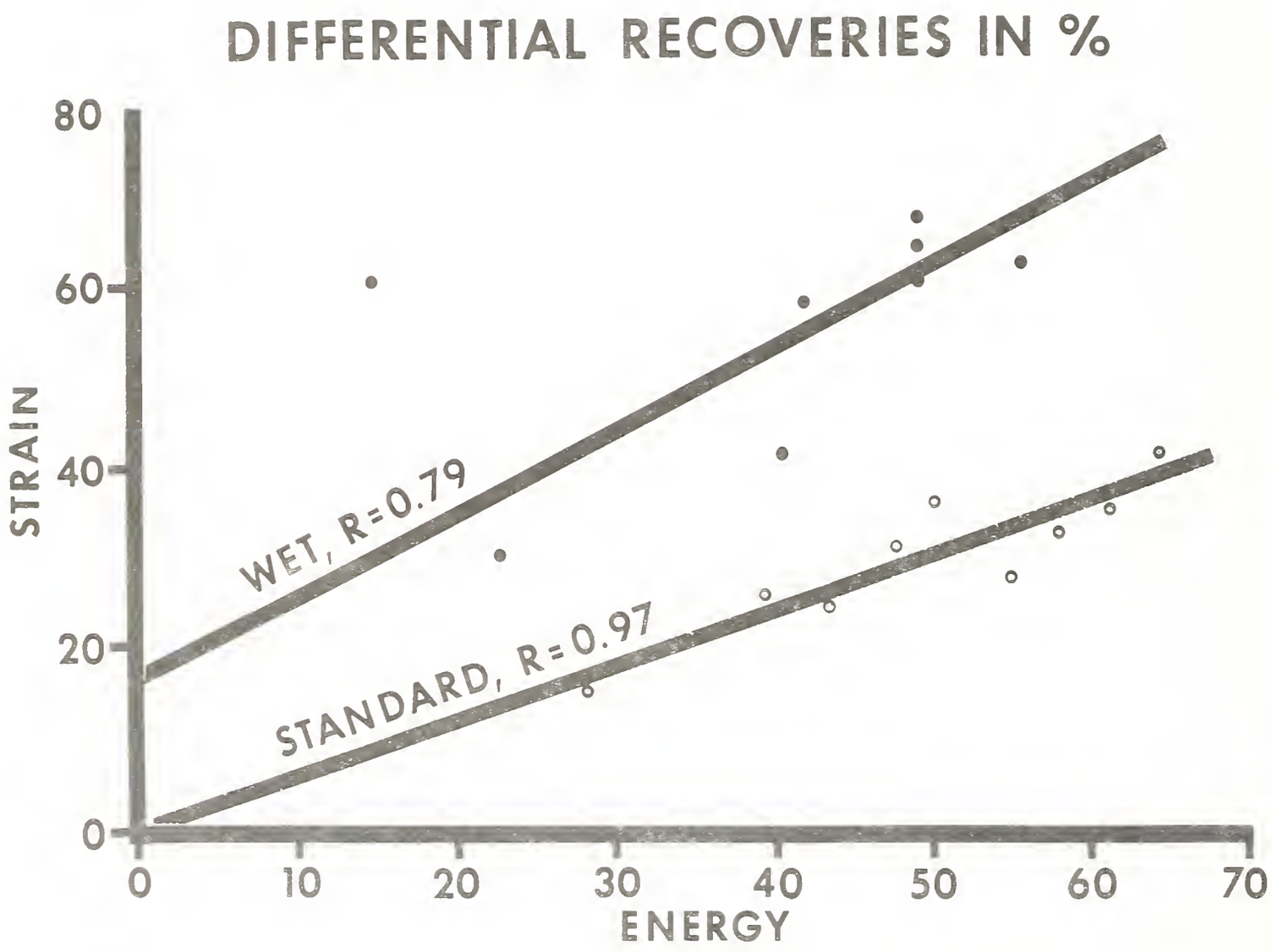

Figure 3. – The increase in tensile strain recovery as a function of the increase in tensile energy recovery for crosslinked single cotton fibers when measured after the deformation due to a 1 gm. load under wet and standard conditions.

Tensile strain recovery for single fibers modified by formaldehyde treatments increases with increasing crosslinkage of the cellulose.

Single cotton fibers, crosslinked in a swollen state, have more flexibility with increased recovery. This combination is displayed, especially under wet test, by individual fibers modified with aqueous formaldehyde using sulfuric acid.

For single cotton fibers, the tensile strain recovery is directly related to the tensile energy recovery if both are measured under the same conditions.

Changes in the mechanical properties of cotton yarns and fabrics caused by chemical treatments are due, in part to the changes in the individual fibers themselves.

ACKNOWLEDGMENTS

The authors express their appreciation to Bethlehem K. Andrews for the chemical treatments.

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CONCEPTS IN CHEMICAL FINISHING OF COTTON: THE REACTIVITY-HYDROLYSIS RELATIONSHIP

by

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ABSTRACT

The reactivity-hydrolysis relationship in chemical finishing of cotton with N-methylol type reactants under acidic conditions are discussed. Theoretical and practical justifications for the relationship are presented to demonstrate that the ease of formation of links is related directly to the ease of hydrolysis of links and relative rates in both directions are predictable based on steric and electronic effects on the resonance-stabilized intermediate. Bond cleavage during hydrolysis has been shown to occur first at the carbon-oxygen bond of the methylol groups whether or not the link was formed from a substituted urea-formaldehyde adduct or a substituted urea-glyoxal adduct.

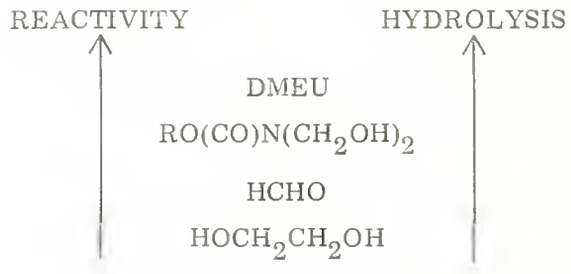
INTRODUCTION

Essentially all durable-press garments containing cellulose have been treated with N-methylol type crosslinking agents to improve the resilience of the cellulosic component. The agent is normally applied or removed under acidic conditions. During crosslinking applications, acidic conditions must not be so strong as to cause hydrolysis of the glycosidic linkages in cellulose; yet, the link to cellulose must be strong enough in many cases to withstand the acid wash used in commercial launderings. In a reversible reaction of this type one could expect that the ease of the forward and reverse reactions are related, i.e., relatively mild aqueous acidic conditions will remove a finish that required only mild acidic catalysis. Similarly, those agents that require relatively strong acid conditions to react with cotton also require strong acidic conditions for the removal of the finish. The primary purpose of this paper is to examine this reactivity-hydrolysis relationship (9, 10) in detail and to provide an adequate justification from both a practical and theoretical viewpoint.

RESULTS AND DISCUSSION

The relationship is illustrated below:

Reactivity-Hydrolysis Relationship



Practical examples of this relationship are evident in two well-known systems: the N-methylol derivatives of ethyleneurea and carbamates. Finishes from dimethylolethyleneurea (DMEU) provide an example of ease of reaction and hydrolysis whereas the carbamates provide an example of agents which form an acid-resistant finish but which require relatively strong conditions in application. Ethylene glycol is an example of a precursor of a durable crosslink, but the crosslink cannot be achieved without at least partial destruction of the cellulose polymer. All N-methylol type crosslinking agents are expected to fall within these extremes or in some cases at the same level as DMEU.

The reactions are considered through a series of reversible steps wherein the formation of the resonance-stabilized intermediate is considered

$$RCONHCH_2OH + H^+ \rightleftharpoons RCONHCH_2\overset{+}{O}H_2 \qquad (1)$$

$$RCONHCH_2\overset{+}{O}H_2 \rightleftharpoons RCONHCH_2^+ + H_2O \qquad (2)$$

$$RCONHCH_2^+ \longleftrightarrow RC\overset{+}{O}NH = CH_2 \quad (3)$$

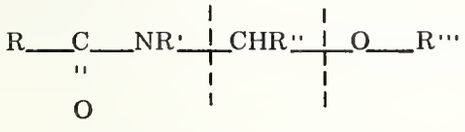
$$RCONHCH_2^+ + CellOH \rightleftharpoons RCONH\text{-}CH_2\overset{+}{\underset{H}{O}}\,Cell \quad (4)$$

$$RCONH\text{-}CH_2\overset{+}{\underset{H}{O}}\,Cell \rightleftharpoons RCONHCH_2O\,Cell + H^+ \quad (5)$$

to be the rate determining step. According to the principle of microscopic reversibility (5), if steps 1 through 5 represent the formation reaction, then steps 5 through 1 should represent the hydrolysis reaction. However, there is considerable work published which suggests that the hydrolysis reaction proceeds by protonation of the nitrogen followed by cleavage of the carbon to nitrogen bond. However, for the relationship to be meaningful theoretically, equation 5 through 1 must represent the actual path of hydrolyses and the ether must hydrolyze at the carbon to oxygen bond as shown in equation 4.

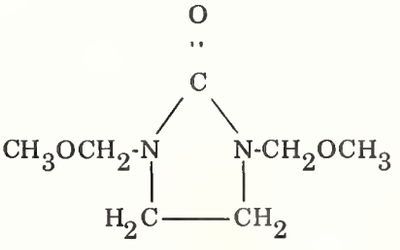
Unfortunately, there are conflicting statements in the literature (3, 6, 8) with regard to the identification of first-formed products from the acid hydrolysis of ethers of N-methylol type amides. Isolable products from the hydrolysis are generally methylenebisamides (13), an experimental finding which does not supply the information necessary to determine the path of the early steps of the hydrolysis.

Initial bond cleavage may be considered to take place at either C-N or C-O bonds as shown by the dotted line in the following:

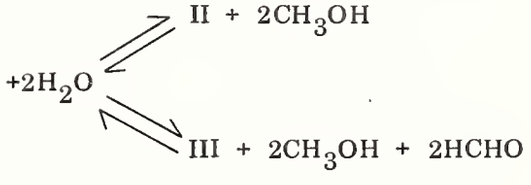


Further, because formaldehyde analyses have been used to obtain rate data for hydrolyses of this type (3, 6, 7), it is desirable to establish the relative rate of aldehyde release (formaldehyde or glyoxal) in comparison with the initial bond cleavage.

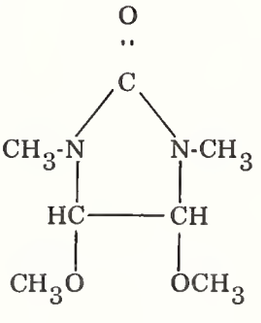
Two substituted, difunctional urea systems were selected for study by means of a nuclear magnetic resonance technique (11) to identify the product as it was formed in the hydrolysis media (dilute hydrochloric acid). Either dimethylolethyleneurea (DMEU or II) or ethyleneurea (III) is the expected nitrogen containing, primary product from the acid hydrolysis of 1,3-bis(methoxymethyl)ethyleneurea (I). Similarly, 1,3-dimethylurea (VI) or 4,5-dihydroxy-1,3-dimethylethyleneurea (V) are the expected



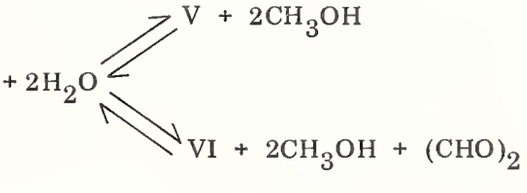
I



product from 4,5-dimethoxy-1,3-dimethylethyleneurea (IV).



IV



Reactants were placed, after mixing at room temperature, in the nmr spectrometer (Varian A60-A) and partial spectra from 2-4 p.p.m. were obtained repeatedly. For the purpose of identifying the products as they were formed (table 1), known peaks from methyl and ring protons of methanol and I-VI, if present, were followed

Table 1. — Partial NMR data of selected compounds in water

Identification of proton	Chemical shift
	P.p.m.
CH_3 in I	3.31
Ring CH_2 in I	3.60
Ring CH_2 in II	3.58
CH_2 in III	3.51
CH_3 in Methanol	3.36
CH_3 in VI	2.71
CH_3 in cis - V	2.78
CH_3 in trans - V	2.83
OCH_3 in IV	3.37
NCH_3 in IV	2.86

during the hydrolysis. Because no major peaks or coupling patterns attributable to an unsymmetrical intermediate were observed, it was assumed that both bonds in the difunctional molecule cleaved at approximately the same time. Once a relatively steady state was achieved, confirmation of peak assignments was obtained by adding selected compounds (methanol or I-VI) to the solutions and noting the changes in the spectra.

Carbon-oxygen bond cleavage was indicated in the hydrolysis of both ethers. The hydrolysis of I at pH 2 proceeded smoothly and rapidly to form II and methanol. A relatively steady state was established in about 2 minutes. Evidence of formaldehyde release was not encountered until the hydrolysis had proceeded for several minutes. The hydrolysis of IV at pH 4 proceeded slowly to form V and methanol. These primary products could not be identified until 7 minutes after the reactants were mixed. Hydrolysis was 50 percent complete in 15 to 20 minutes. Nearly all of IV was converted to V after 35 minutes. There was no evidence of formation of VI (or glyoxal) during the 45 minute period that the partial nmr spectra were taken.

Therefore, we may represent the hydrolysis reaction as proceeding by carbon-oxygen bond cleavage to form an N-methylol type compound. In those cases where R '' = H, formaldehyde is released in a slower step to form the amide. The

$$RCNR'CHR''OR'''+H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} RCNR'CHR''OH+R'''OH$$

amide, in turn, reacts rapidly with the N-methylol amide to form ultimately the expected methylenebusamides. Confirmation of these

$$RCNR'CH_2OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCNHR' + HCHO$$

steps was obtained by adding III to an equilibrating mixture of I and II (predominately II) at pH 2 and observing the rapid changes in the nmr spectra of the materials. The predominant peaks attributable to II and III disappeared almost immediately (about 2 minutes required).

The rate of release of glyoxal from V was too slow to follow under the selected reaction conditions. The addition of 1,3-dimethylurea (VI) to an equilibrating mixture of IV and V did not have an immediate effect upon that equilibrium. A tetracyclic acetal, composed of two molecules of V and one of glyoxal, has been isolated from a similar system but only after several days time (2).

In summary, to this point, carbon-oxygen bonds are the first cleaved in acid hydrolysis of ethers of N-methylol type amides (formed from adducts of ureas with formaldehyde or glyocal). In addition, subsequent release of the aldehyde is a significantly slower reaction and free formaldehyde analyses cannot be used to establish hydrolysis rates for these ethers.

These data provide the theoretical justification necessary for the concept, i.e., the reactivity-hydrolysis relationship, herein described. However, it must be realized that the

concept applies to reversible systems and, therefore, will often exclude those systems wherein the agent polymerizes, releases formaldehyde and/or forms several types of crosslinks, or becomes involved in other reactions which destroys the reversibility of the system.

It is not the purpose of this paper to fit a large number of N-methylol agents into a list relating steric and electronic factors to reaction or hydrolysis rates. Some work of this nature is already available. References of particular interest are those (1, 4, 8, 12) wherein a wide spectrum of rates of hydrolysis were studied, i.e., fabrics finished with agents from ureas, carbamates, acetamides, formamides, and similar amides were compared. Generally, most relationships are obtained through the consideration of only electronic factors; the better relationships are obtained through the use of homologous series wherein simple substitution, e.g., CH_3 for H, is used. Complications or inequities may be encountered during application of this concept to practical problems, but a search for the cause, physical or chemical, can be expected to develop much useful information in addition to providing additional justification for the concept.

Practical implications and applications are numerous. For example, a very active crosslinking agent will not form a hydrolysis-stable cellulose derivative if the reactions are reversible. Similarly, obtaining a designed hydrolysis-stable crosslink may not be possible in practice, unless a nonreversible sequence of steps are used to form the cellulose derivatives. Further, one may use the relationship to help identify the product(s) of some cellulose-N-methylol crosslinker reactions, i.e., hydrolysis of the product(s) could suggest the presence of a second crosslink, for example, from formaldehyde. These and many other benefits are obtainable through application of this useful concept.

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THIRD SESSION: A.M. Sookne, Burlington Industries, Inc., Greensboro, N.C., Chairman

STUDIES IN SWELLING OF CELLULOSE: PART I. INTRACRYSTALLINE SWELLING AND DECRYSTALLIZATION IN ZINC CHLORIDE-TREATED COTTON CELLULOSE

by

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ABSTRACT

Changes in the fine structure of cotton cellulose taking place during treatment with aqueous solutions of zinc chloride under different conditions of concentration and temperature have been studied. Treated samples have been examined for changes in physical characteristics such as refractive index, density, infrared crystallinity index, breaking strength, and extent of swelling as well as structural changes taking place, from measurements of accessibility to moisture sorption, acid hydrolysis, and formylation. Results indicate that zinc chloride solutions at critical concentrations of 65 to 70 percent (w/w) bring about considerable swelling and decrystallization and the extent of changes produced are dependent on the conditions of treatment. Lateral-order distribution of cotton cellulose treated with aqueous zinc chloride solutions indicate changes depending on the concentration used and time and temperature of treatment. Evidence of formation of specific hydrates in aqueous solutions of specific concentrations of zinc chloride has been obtained from conductivity measurements and UV absorption characteristics. UV and IR spectroscopic measurements indicate the formation of complexes between zinc chloride and cellobiose or cellulose.

Aqueous zinc chloride solutions have been found to be swelling agents for cellulose. Letters (6) appears to be the first to indicate that 63 percent aqueous solution of zinc chloride had enormous swelling action on cotton cellulose, while Smirnov (16) indicated that in addition to the concentration of 63 percent, aqueous zinc chloride solution of 75 percent concentration was also effective in bringing about considerable swelling. On the other hand, Kasbekar and Neale (4) observed progressive increase in shrinkage and swelling of cotton yarn as concentration of zinc chloride in the aqueous solution was increased from 10 to 74 percent. Patil and others (12) indicated that zinc chloride solutions at critical concentrations of 64 and 70 percent had profound decrystallizing effect on cotton cellulose and the extent of decrystallization was dependent on time as well as temperature of treatment. These workers, however, did not put forward any explanation regarding such behavior.

In the present study, a critical evaluation of the swelling and decrystallizing action of acqueous solutions of zinc chloride of different

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concentrations at the temperatures of 20° and 35°C. has been made. Specific characteristics of the aqueous solutions of zinc chloride have been examined and evidence is put forth to indicate that the intracrystalline swelling and decrystallization of cotton cellulose under different conditions of treatment with zinc chloride solutions is due to the nature and extent of formation of specific hydrates in the aqueous solution rather than due to formation of different types of complexes between zinc chloride and cellulose.

EXPERIMENTAL PROCEDURES

Good quality long staple Sudanese cotton in loose form was purified according to the standard procedure. Zinc chloride used was of C.P. grade.

Preparation of swollen cellulose samples:-- Purified cotton cellulose was treated with aqueous solutions of the swelling agent at different concentrations for 1 and 5 hr. at 20° C. and 1 hr. at 35° C. At the end of the treatment, samples were washed repeatedly with distilled water to make them free from the swelling agent and water was removed by displacement first by dry methanol and then by cyclohexane so that collapse in structure of swollen cellulose, caused by sudden removal of water, was avoided. Samples were air-dried and conditioned at 75 percent R.H. at 30° C.

Determination of physical, chemical, and fine structure characteristics of cotton cellulose--Strength of flat bundles of fibers at nominal zero gage were determined on a Stelometer Strength tester. Relative breaking strength of each swollen sample was calculated considering the breaking strength of untreated cotton at 100 percent.

Density measurements were made in a density gradient tube at 25° C. by use of a mixture of a carbon tetrachloride and zylene according to the method recommended by Preston and Nimker (13).

Refractive indices of swollen samples were measured at 30° C. by the well known Becke line (8) method using Leitz Ortholux-Pol polarizing microscope with heating stage.

Infrared crystallinity index was calculated by the method suggested by O'Connor and others (11), infrared spectra being obtained by KBr-pallet technique, using Perkin-Elmer model 21 double beam infrared spectrophotometer with sodium chloride optics.

Moisture regain of the sample was determined at 75 percent R.H. and 30° ±1° C. under conditions of adsorption.

Extent of swelling was measured by the propanol-2 retention method suggested by Andrews and Oberg (1).

Accessibility of the swollen samples to acid hydrolysis was obtained using mild conditions of hydrolysis viz. 1 N HC1 at 30° C. as employed by Sharples (15) and comparing the rate of hydrolysis with that for cellopentose under identical conditions. Formylation method suggested by Marchessault and Howsmon (7) was also employed to determine accessibility. Recently Heath and Jeffries (3) have questioned the validity of formylation technique as a means of studying order and disorder in cellulose as they found that formic acid produced ordered, inaccessible regions in disordered cellulose. However, it was noticed that in partly ordered cellulose, formic acid had little effect on the order and therefore for the present investigations where inaccessible region in the swollen samples are sufficiently high, formylation technique may be considered satisfactory as a measure of accessibility.

Lateral-order distribution in swollen samples was obtained from the results of formylation carried out at different temperatures of 5 to 65° C. and calculating accessibilities at these respective temperatures.

Electron microscopic examination and X-ray diffraction analysis were carried out for only those samples that were treated at the most effective concentration of the swelling agents.

For electron micrographs, the sample was beaten in water in a blender. The slurry, after drying on a specimen grid, was appropriately shadowed with Au-Pd and examined under an electron microscope. The microfibril width and thickness were determined by the method described by Preston (14).

X-ray photographs were taken with Cuk ∞ radiation at 35 KV and 20 mA, collimated to a beam 0.5 mm. in diameter with a specimen to plate distance of cm. calibrated against silver diagram. The crystallite dimension, D (002) in A, ⊥ to the plane hkl was determined using Scherrer's equation (5).

Conductivity measurements of zinc chlorider solutions.—Conductivity measurements were carried out on Phillips PR 9500 type conductivity bridge at 20 and 35° C. at different concentrations of the swelling agents.

Determination of UV absorption spectra:—Ultraviolet absorption spectra of aqueous zinc chloride solutions and of zinc chloride—cellobiose solutions were obtained on Beckmann Model DK-2 recording spectro-photometer.

RESULTS AND DISCUSSION

Results of the present studies reveal that characteristics of cotton cellulose, such as density, birefringence, infrared crystallinity index, moisture regain, flat bundle strength, extent of swelling, accessibility to acid hydrolysis and formylation, and lateral-order distribution of fibre substance are altered depending on the concentration of the zinc chloride solutions used (tables 1 and 2; figures 1 and 2).

In general, there are four distinct stages in the structural changes brought about in cotton with increasing concentration of aqueous zinc chloride solutions during treatment of 20° C. for 1 hr. Up to a concentration of about 55 percent (w/w), there is little change in these characteristics, between 55 and 65 percent concentrations considerable swelling and marked changes in the other fibre characteristics take place and at a concentration of 68 percent, there is comparatively little change as compared with untreated cotton. At 70 percent concentration, however, there is once again enhanced swelling and decrystallization followed by a sharp rise towards the original values of fibre characteristics around the saturation point. When swelling time is increased from 1 hr. to 5 hr. at 20° C., the pattern of behavior with respect to changes in the fibre characteristics at different concentrations of zinc chloride solutions is the same as that for 1 hr. treatment except that the changes observed are more pronounced. When the temperature is raised to 35° C. although maximum changes in fibre characteristics are observed at the same critical concentrations of zinc chloride viz., 65 and 70 percent, there is a reversal in the extent of modification brought about at these two concentrations, changes are more pronounced at 70 percent concentration as compared with those at 65 percent.

Cotton on treatment with aqueous zinc chloride solution of 70 percent concentration at 35° C. for 1 hr. loses its fibrous form and gives a powder diagram due to complete breakdown of crystal structure. At the intermediate temperature of 28° C., the behavior with respect to changes brought about in the fibre characteristics is intermediate between those obtained at 20° C. and 35° C. at both the critical concentrations of 65 and 70 percent.

When swelling treatment is carried out at 20° C. for 1 hr. with different concentrations of zinc chloride (figure 3), the low-order region first decreases slightly from 19 percent to 15 and 17 percent as the concentration is increased to 45 and 60 percent, respectively. But, at a concentration of 65 percent, there is a rapid increase to about 30 percent in this region followed by once again decrease to 15 percent, when the concentration of zinc chloride used is increased to 68 percent. At a concentration of 70 percent, the proportion of low-order fraction is about 22 percent, which decreases once again to that of original cellulose level of 18 percent when the zinc chloride concentration used is 80 percent. With respect to intermediate—order fraction, the pattern is the same and at both the concentrations of 65 to 70 percent zinc chloride, the magnitude of this order region is 25 to 18 percent, respectively, as compared with the value of about 12 percent in the case of untreated cotton cellulose. The high-order fraction decreases from about 69 percent for the untreated sample to about 45 percent for the sample treated with 65 percent zinc chloride solution. It gives a value of 71 percent at the 68 percent concentration, again decreases to 60 percent at 70 percent concentration, and comes back to the value of 71 percent at the zinc chloride concentration of 80 percent (fig 3). Thus, similar to the behavior observed with respect to density measurements, birefringence, infrared crystallinity index, and accessibility to

Table 1. — Changes in the fine structure of cellulose due to swelling with zinc chloride solutions under different conditions.

Time and Temp. of treatment	Zinc chloride (w/w)	Birefringence for sodium D line at 30°C. n n	Density	Infrared crystallinity index	Moisture regain	Relative Breaking strength	Accessibility		Extent of swelling
							Acid Hydrolysis	Formylation	
	Pct.		G./cm.^{3}		Pct.	Pct.	Pct.	Pct.	Cm.^{3}/100g.
1 Hr.	0	0.0460	1.5502	2.9	8.33	100	15.0	30.6	17.2
	20	—	1.5501	—	7.87	—	14.2		—
20°C	40	1.0477	1.5507	3.3	6.78	100		28.8	14.6
	45	0.0469	1.5505	3.5	7.11	103	12.8	23.9	12.3
	50	0.0428	1.5548	—	8.00	100	12.0	—	10.2
	55	0.0452	1.5505	—	8.51	90	25.5	—	18.1
	60	0.0461	1.5425	2.6	8.63	93	32.9	30.5	—
	65	0.0420	1.5288	1.5	10.28	66	39.7	55.2	54.7
	68	0.0475	1.5504	2.8	8.83	97	16.8	28.5	14.1
	70	0.0455	1.5350	2.3	9.49	90	25.7	39.6	30.5
	75	0.0460	1.5506	—	8.35	90	14.7	22.1	16.7
	80	0.0536	1.5507	2.6	7.92	98	15.2	28.6	13.2
5 hr.	20	—	1.5516	—	8.23	95	14.0	29.0	14.5
	40	—	1.5520	—	8.03	101	14.5	27.9	12.2
20°C.	45	—	1.5567	1	8.20	99	12.5	22.1	12.4
	50	—	1.5588	—	—	—	—	—	—
	55	—	1.5489	—	9.25	—	29.2	28.2	18.8
	60	—	—	—	—	—	37.1	32.8	—
	65	—	1.5251	—	13.13	72	41.8	58.7	61.5
	68	—	1.5500	—	10.91	87	19.5	30.9	16.7
	70	—	1.5360	—	12.75	81	26.7	43.2	35.0
	75	—	1.5516	—	10.44	84	16.8	—	18.7
	80	—	1.5500	—	10.48	—	15.9	32.8	17.4
1 hr.	20	—	1.5501	—	9.00	98	15.1	35.0	19.9
	40	—	1.5481	—	8.82	95	—	36.0	24.0
35°C.	45	—	1.5481	—	8.85	100	16.2	37.9	24.5
	50	—	—	—	—	—	—	38.1	—
	55	—	1.5416	—	8.31	—	36.4	39.0	39.0
	60	—	—	—	—	—	41.2	50.1	—
	65	—	1.5090	—	13.61	—	43.1	63.7	64.2
	68	—	1.5221	—	10.07	83	35.8	45.9	44.1
	70	—	1.4902	—	14.45	—	68.2	85.3	80.9
	75	—	1.5178	—	13.36	—	60.5	44.4	41.5
	80	—	—	—	13.26	—	51.7	44.8	40.7

Table 2. — Changes in the fine structure of cellulose caused swelling with zinc chloride solutions at 28° C. for 1 hr.

Zinc chloride	Density	Moisture regain,	Accessibility by formylation,	Extent of swelling,
Pct. (w/w)	G/cm.^{3}	Pct.	Pct.	CM^3/100 g.
0	1.5502	8.33	30.6	17.2
20	1.5500	8.45	31.9	19.0
40	1.5481	8.60	32.3	20.4
45	1.5475	8.65	34.0	21.4
50	1.5462	8.81	34.8	-
55	1.5442	9.20	38.1	26.1
60	1.5400	10.00	45.1	40.1
65	1.5218	12.45	60.2	60.5
68	1.5448	8.94	35.8	25.7
70	1.5200	12.40	62.1	61.3
75	1.5420	9.60	40.0	23.0
80	1.5424	9.56	40.2	23.1

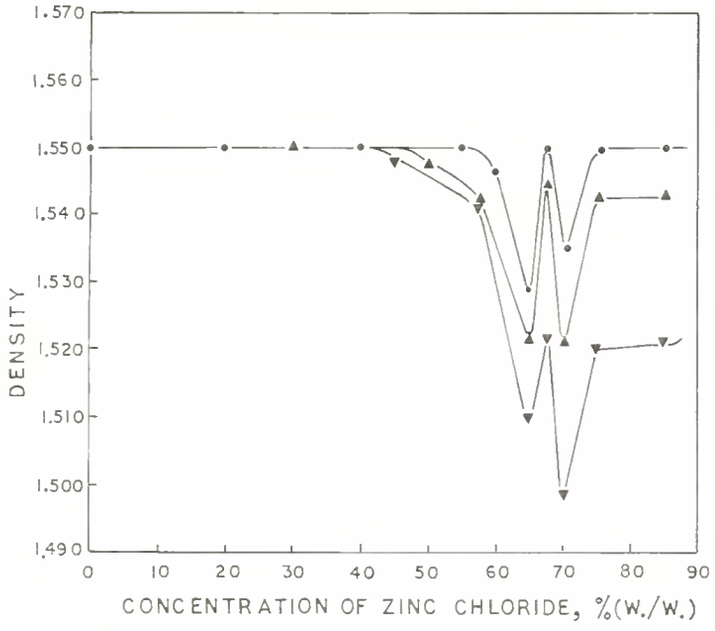

Figure 1. — Relation between density of swollen cotton cellulose and concentration of zinc chloride solutions at different temperatures for 1 hr. - ● - 20° C., - ▲ - 28° C., - ▼ - 35° C.

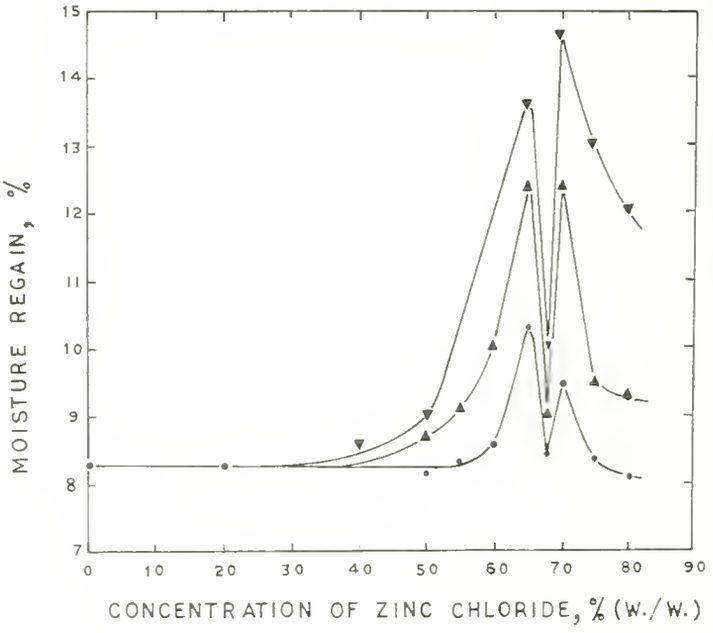

Figure 2. — Relation between moisture regain of swollen cotton cellulose and concentrations of zinc chloride solutions at different temperatures for 1 hr. - ● - 20° C., - ▲ - 28° C., - ▼ - 35° C.

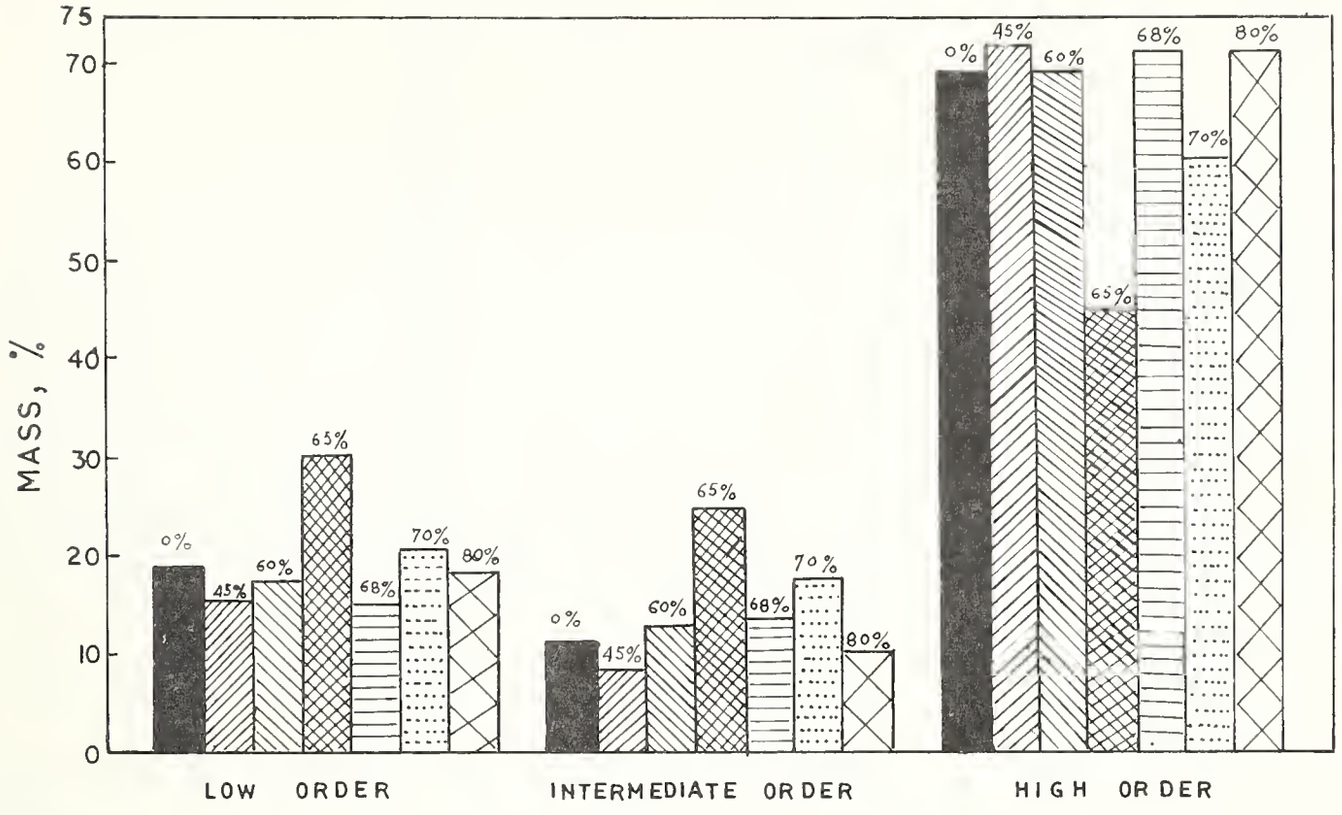

Figure 3. — Later-order distribution histograms of cotton treated with zinc chloride solutions at 20° C. for 1 hr.

moisture, formylation or acid hydrolysis, changes in the mass-order distribution in the fiber substance run parallel at equivalent concentrations of zinc chloride solutions.

With respect to mass order distribution in cotton cellulose samples swollen with zinc chloride solutions at 35° C. for 1 hr., the low-order fraction increases from 19 to 37 percent as the concentration is increased to 65 percent. This is followed by a decrease of 24 percent at 68 percent concentration, again increase to 57 percent at 70 percent concentration and once again a decrease to 22 percent at 80 percent concentration. The same pattern is observed with respect to intermediate-order fraction except that the magnitude is less as compared with the low-order fraction. The high-order fraction decreases from 69 to 36 percent as the concentration of zinc chloride is increased progressively to 65 percent. At 68 percent concentration, high-order fraction is more viz. 54 percent, while at 70 percent concentration, there is a rapid decrease in the high-order fraction to about 15 percent followed by an increase to 55 percent at 80 percent zinc chloride concentration (fig 4). These results are in conformity with the decrystallizing behavior of zinc chloride solution at 35° C. on treatment for 1 hr. as is reflected in the physical and chemical changes brought about in the cotton fibers.

The effect of considerable intracrystalline swelling and decrystallization brought about by zinc chloride solution (65 percent, 20° C., 1 hr.) is reflected in electron micrographs and x-ray diffractograms. As compared with the untreated sample (figure 5) having characteristic texture with linear parallelization of microfibrils, treatment with zinc chloride seems to be severe. The parallel arrangement and texture of

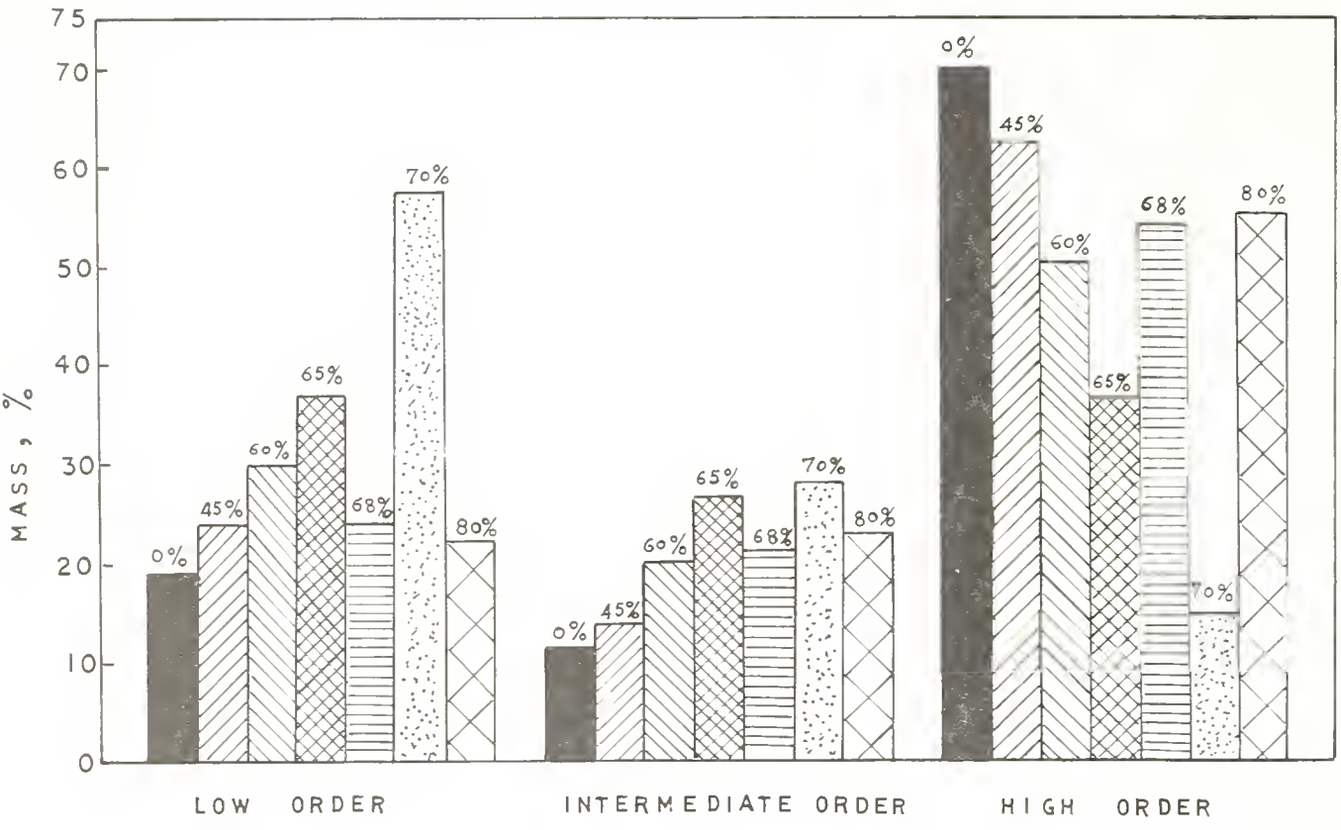

Figure 4. — Later-order distribution histograms of cotton treated with zinc chloride solutions at 35° C. for 1 hr.

microfibrillar mass are destroyed and the swollen microfibrils have dimensions of 240 x 120 A (figure 6) as compared with 110 x 25 A in the untreated specimen. The crystallite dimension of the plane D002 is also reduced from 49.05 A in untreated sample to 33.22 A in zinc chloride swollen sample, confirming the decrystallization effect of the swelling agent.

Characteristics of aqueous zinc chloride solutions: With a view to find out the reasons for this unique behavior of appreciable swelling and decrystallization at specific concentrations of zinc chloride in the aqueous solutions, conductivity measurements and spectral investigations were carried out on aqueous zinc chloride solutions of different concentrations at 20° and 35° C. Conductivity measurements reveal that there are two breaks in the plots correlating specific conductivity with the amount of zinc chloride present in the solutions both at 20° and 35° C., and these breaks take place at 65 and 71 percent (w/w) zinc chloride concentrations (fig 7). To determine the changes occurring in the aqueous solutions of zinc chloride due to the hydrolysis of zinc chloride as a function of time, conductivity measurements of these solutions were taken at an interval of 1 hr. It was observed that values of specific conductivity for each solution remained practically unaltered over a period of 5 hours.

Zinc chloride solutions show strong absorption in the untraviolet region of 255 mμ and also in the short wave-length region. Absorption intensity as 255 mμ is greatly reduced at concentrations at 65 to 70 percent, and absorption maximum falls within the range of optical density below 1.5, path-length remaining the same throughout at 1 cm. At any concentration either below 65 or between 65 and 70 percent, the 255 mμ peak intensity is very high (figure 8). Both the results of conductivity measurements and spectral

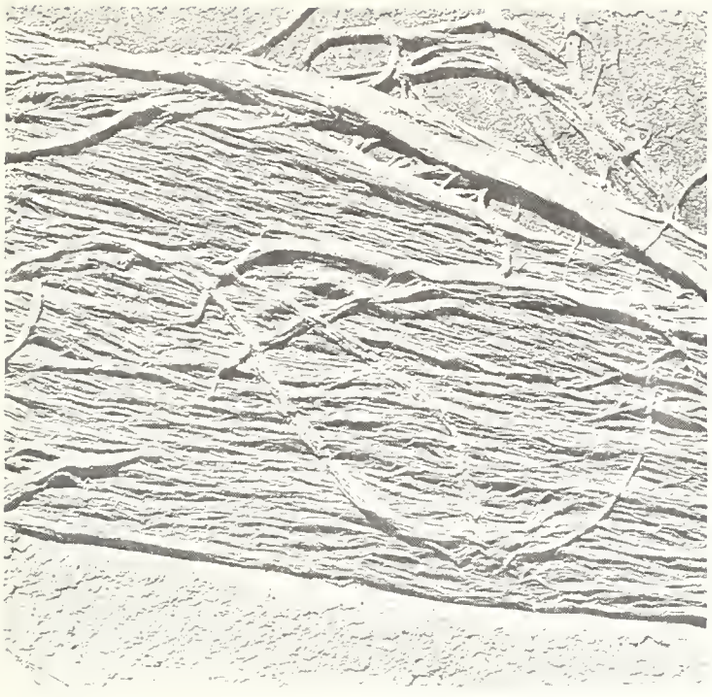

Figure 5. — Electron micrograph of untreated cotton. Shadowed Au-Pd. 37,600 X.

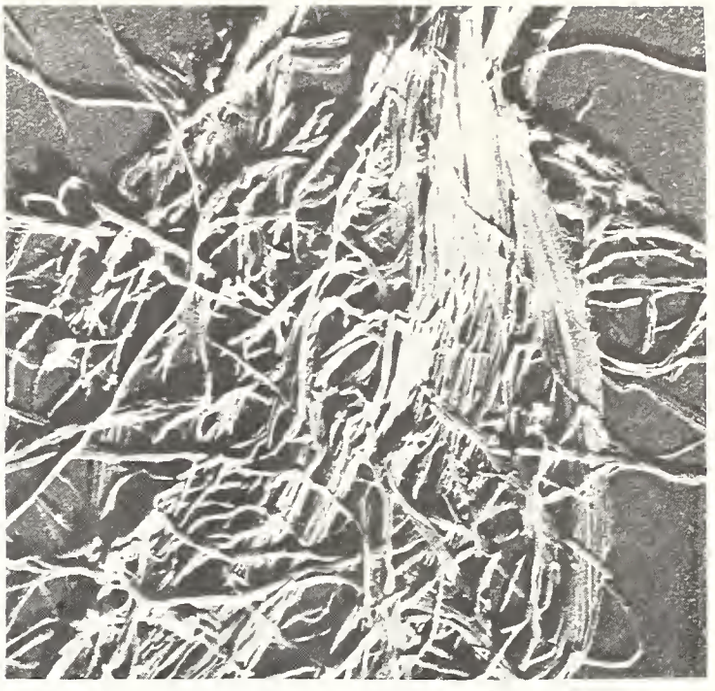

Figure 6. — Electron micrograph of cotton treated with 65 percent zinc chloride at 20° C. for 1 hr. Shadowed Au-Pd. 26,300 X.

analysis indicate that there is some specific interaction between the molecules of water and molecules of zinc chloride at the critical concentrations of 65 to 70 percent. The 255 mμ peak may presumably arise out of the specific excitation of electrons of Zn ion in zinc chloride, which are influenced by the solvent molecules at these two concentrations only, so that the excitation energy is increased, thus reducing the intensity of 255 mμ peak. The effect of temperature indicates that the nature of this interaction or hydrate characteristics of 70-percent solution has been observed at 35° C., which is not predominantly present at 20° C. It is, however, observed that there is only a slight increase in the 255 mμ peak at 35° C. for 65-percent zinc chloride solutions, which goes to show that the hydrate characteristic of 65-percent solution is still present in the solution, but the concentration is only slightly less. The molal proportions of zinc chloride and water at 65-percent and 70-percent concentrations are 1:4 and 1:3, respectively, and it is very likely that $ZnC1_2.(H_2O)_4$ and $(ZnC\ 1_2)_2.(H_2O)_6$ hydrates are predominantly present at these concentrations, respectively. The reduction in intensity of 255 mμ peak is characteristic of hydrate formation. At 68-percent concentration, where it is expected that the solution would show an equilibrium mixture of the two hydrates, the optical density of 255 mμ peak at this concentration goes beyond the range, indicating that 68-percent solution does not show formation of specific hydrates predominantly. These observations run parallel with swelling and decrystallizing behavior of cotton cellulose under conditions of 65-, 68-, and 70-percent concentrations at 20° and 35° C.

It is well known that metallic cations are hydrated in their salt solutions because of the lone pair of electrons in oxygen atom of the water molecules, and they form co-ordinate bonds with the cations giving rise to stable hydrates similar to polynuclear complexes. It has been observed that molecules of water form different spheres around the metal ion and these different spheres have different activity. According to Neale (10), more the number of water molecules present into the metal hydrate the more effective is the hydrate with respect to penetration and breaking the hydrogen bonds between the cellulose chains. Zinc chloride forms tetrahydrate at 65-percent concentration. Molal proportion of zinc chloride and water at 70-percent concentration is 1:3. Zinc has maximum coordination number 6 and, therefore, it can only form either trihydrate or

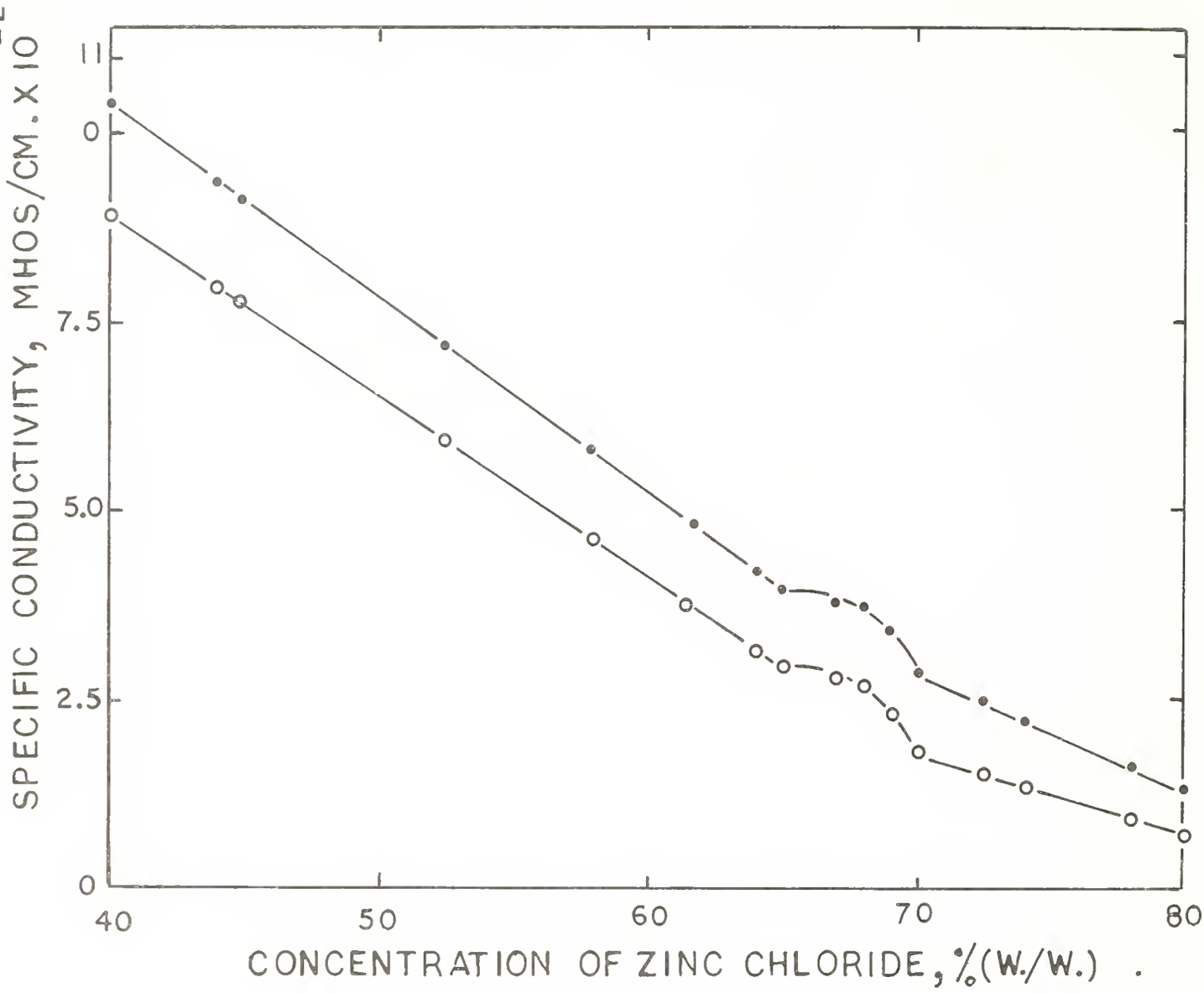

Figure 7. — Relation between specific conductivity and concentrations of zinc chloride solutions at different temperatures. ● - 0 - 20° C., - ● - 35° C.

hexahydrate. Thus, the possible hydrate at 70-percent concentration is $(ZnCl_2)_2.(H_2O)6$. Mylius and Dietz (9) have actually isolated zinc chloride tetrahydrate ($ZnCl_2.4H_2O$) as large prismatic crystals by cooling a 65.4 percent aqueous zinc chloride solution below -30°C., while hygroscopic rhombic plates and cubic crystals of trihydrate of zinc chloride ($ZnCl_2.3H_2O$) resembling sodium chloride crystals have been obtained by Enger (2) by keeping a 70.5 percent solution of zinc chloride at 0° for C. for 24 hr. It is quite likely that there may exist some other forms of hydrate to a certain extent in the aqueous solutions of zinc chloride and the above two main types of hydrate along with other types of hydrate, free zinc ions, and free water molecules form an equilibrium phase. The effectiveness, with respect to swelling and decrystallization, of an aqueous solution of zinc chloride of a particular concentration is dependent on the predominance of either of the two hydrates present in the solution at a particular temperature. It is quite likely that the distribution of two types of hydrate in the zinc chloride solutions at different temperatures may be different. It is

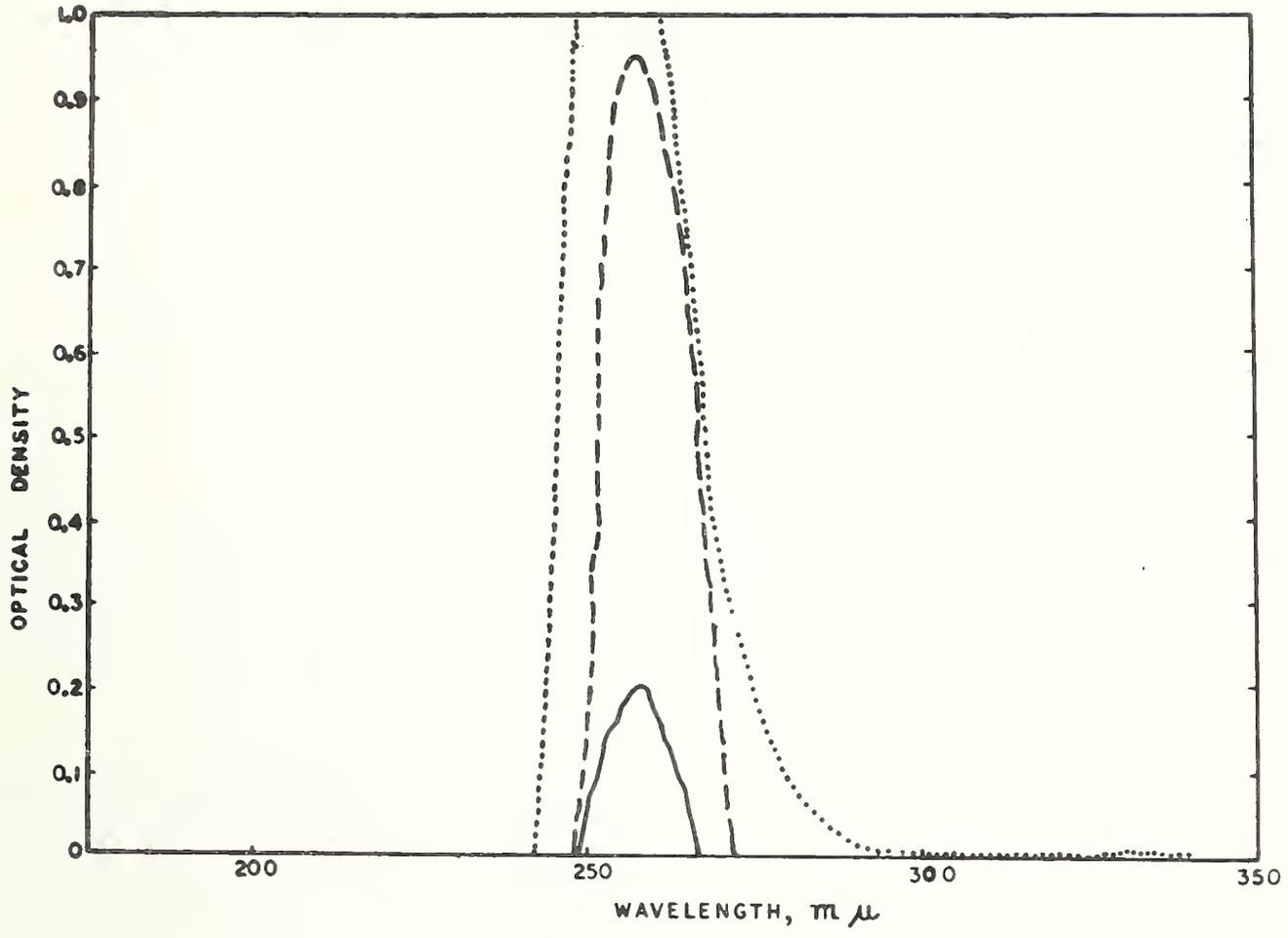

Figure 8. — Ultraviolet spectra of aqueous zinc chloride solutions of different concentrations at 35° C. _____65 percent, ...68 percent _____70 percent

possible that at 20° C., $ZnCl_2.(H_2O)_4$ is in predominance at 65-percent concentration over $(ZnCl_2)_2—(H_2O)_6$ at 70 percent concentration and, therefore, at 20° C., 65-percent zinc chloride solution is more effective. On the other hand, at 35° C., the distribution of the hydrates in the solution is altered and $(ZnCl_2)_2(H_2O)_6$ may become more predominant at 70-percent concentration over $(ZNCl_2 . (H_2O)_4$ at 65-percent concentration leading to greater effectiveness of 70-percent solution as compared with that of 65-percent at this temperature. The ineffective behavior of 68-percent zinc chloride solution can be explained on the basis of distribution method of hydrates. $ZnCl_2 . (H_2O)_4$, which is in maximum quantity at 65-percent concentration, goes on decreasing as the concentration is increased and at about 68-percent concentration this hydrate is present in a limited quantity. With respect to the second hydrate, namely, $(ZnCl_2)_2(H_2O)_6$, it may also be present in a very small quantity at this concentration and its proportion increases as the concentration of zinc chloride is increased beyond 68 percent. At 70 percent concentration it reaches a maximum and beyond this concentration of zinc chloride solution, this hydrate once again decreases in quantity. Thus, at 68-percent concentration, the amount of both the types of hydrate is small and hence the solution at this concentration is not effective with respect to swelling and decrystallization of cotton cellulose. Beyond 70-percent concentration there is not sufficient quantity of water to complete ionization of zinc chloride and for preswelling of cellulose structure required for penetration of the hydrate inside the fibre substance and, therefore, solutions beyond 70-percent concentration are again less effective with respect to swelling and decrystallizing effect.

To determine the homogeneity or otherwise of aqueous solutions of zinc chloride at different concentrations, columns of these solutions at 65-, 68-, and 70-percent concentrations, were set up and allowed to stand for several days at a constant temperature (35° ±0.1° C.). Four arbitrary layers from these columns were carefully separated and UV absorption characteristics of each layer were recorded. It is observed that different layers of 65- and 70-percent aqueous zinc chloride solutions show different absorption characteristics, indicating that there is phase-separation in the column at these concentrations, while 68-percent solution does not show phase-separation of the heavy hydrated ions, and the absorption of the solutions from each of the four layers is more or less the same (table 3). Thus, under conditions of 65- and 70-percent concentrations, a gradient is

Table 3. — UV absorption of zinc chloride solutions of different concentrations

Zinc chloride, Pct. (w/w)	Absorption for the peak at 210 mμ, pct.			
	Layers			
	1[1]	2	3	4[2]
65	70.5	69.5	64.5	37.8
68	48.0	-	47.0	45.0
70	73.0	53.5	-	40.5

[1] Bottom. [2] Top.

set up leading to phase-separation depending on the concentration of hydrated zinc ions, free zinc ions, free chloride ions, and free water molecules. It appears that under conditions of 68 percent zinc chloride solutions, no specific type of hydrate is predomenantly present.

Investigation of complexes between cellobiose of cotton cellulose and aqueous zinc chloride solutions:—To find out whether the swelling and decrystallizing behavior observed in the present studies at different concentrations of zinc chloride in the aqueous solutions was due to the state in which zinc chloride is present in the solution, or whether different types of complexes are formed between cellulose and zinc chloride solutions of different concentrations, interaction of cellobiose and aqueous solutions of zinc chloride at various concentrations was studied by recording spectra in the ultraviolet region. Cellobiose was selected as the model compound. It is found that cellobiose, both under conditions 65- and 70-percent zinc chloride solutions, gives a peak at about 30 mμ, in addition to the 255 mμ zinc chloride hydrate peak, while at intermediate 68 percent concentration, the intensity of the 300 mμ cellobiose-zinc chloride complex peak is very small and it is absent at all the concentrations lower than 65 percent (fig 9). The intensity of 300 mμ band caused by complex formation is

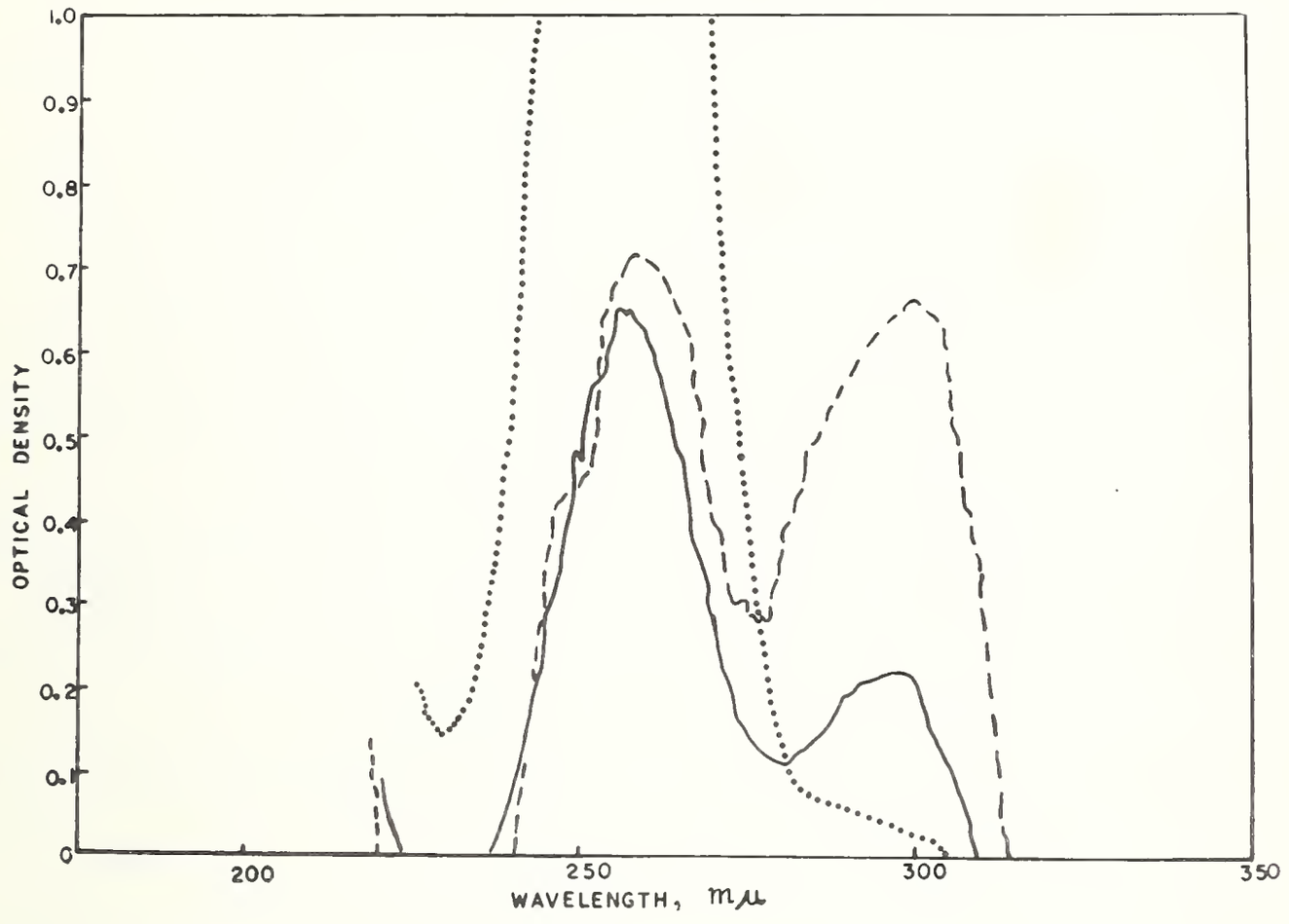

Figure 9. — Ultraviolet spectra of cellobiose complex with zinc chloride solutions of different concentrations at 35° C.
———— 65 percent, ... 68 percent, - - - - - - - 70 percent.

stronger for 70-percent zinc chloride solution as compared with that for 65-percent solution, although the wavelength of maximum absorption remains the same, indicating that only one type of complex formation of cellobiose at both these concentrations is likely to take place. The cellobiose complex not formed with 68-percent solution goes to show that presence of a specific hydrate is a prerequisite for the interaction with cellobiose molecule.

Further evidence of complex formation of similar type is available from infrared studies of cotton cellulose treated with 65- to 70-percent aqueous solutions of zinc chloride. In the case of samples prior to washing-off of zinc chloride, a band at 1630 cm^{-1} (6.1 μ) present in the spectrum of cotton cellulose is shifted to 1605 cm^{-1} (6.2 μ), the band at 1429 cm^{-1} (7μ) is completely suppressed, and 1275 cm^{-1} (7.8 μ) band is split into two bands at these critical concentrations. However, when zinc chloride is completely removed from the swollen sample, infrared characteristics of cellulose I are reverted except that in the case of samples where swelling and decrystallization is appreciable, the band at 1275 cm^{-1} (7.8 μ) is completely suppressed (figure 10). Absorption in the region near about 1429 cm^{-1} (7 μ) has been attributed to the CH_2-bending and as the absorption at these wavebands is interfered in the zinc chloride-treated samples before washing, it is likely that the complex-formation between cellulose and hydrates of zinc ions takes place at the primary alcoholic groups in the glucose unit. The complex gets broken on subsequent washing of the samples and, therefore, absorption characteristics of the original cotton at these wavebands are reverted. 1275 cm^{-1} (7.8 μ) band in the cellulose spectrum is the characteristic band of CH_2-bending, and as this band is suppressed in the case of zinc chloride treated and subsequently washed sample, the CH_2 group in the glucose unit in the cellulose chain molecules has been affected by zinc hydrates present in the aqueous solutions under conditions of 65- and 70-percent concentrations. Greater the extent of swelling and decrystallization, higher is the suppression of the 1275 cm^{-1} (7.8 μ) band in the swollen samples. In the case of cotton cellulose treated with 68 percent aqueous zinc chloride solution and before washing, no changes in IR spectra, unlike those observed in case of treatment with 65- and 70-percent concentrations, are noticed and no complex formation between cellulose and zinc chloride could be detected.

Grateful thanks are due to Professor R.D. Preston, University of Leeds, for giving facilities to one of us (S.M.B.) for taking the electron micrographs. Thanks are also due to the Director, Cotton Technological Research Laboratory, for the permission to publish this paper.

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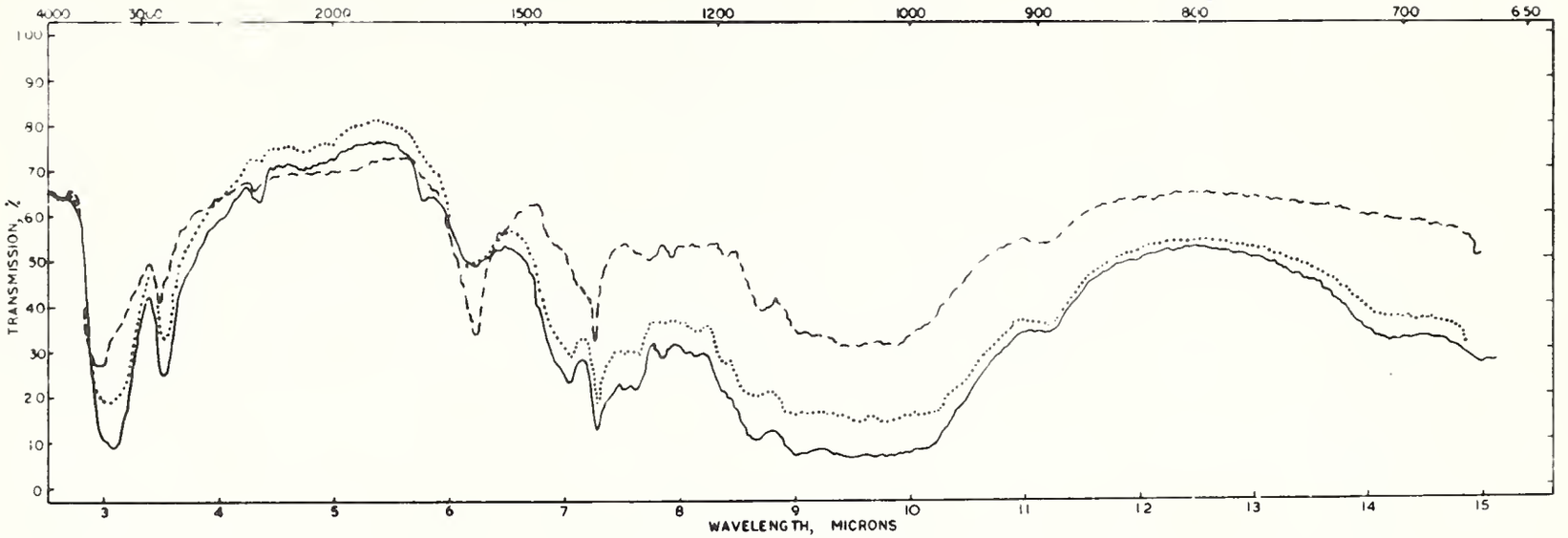

Figure 10. --Infrared spectra of cotton treated with 85 percent zinc chloride at 20° C. for 1 hr.
——— untreated,
---------- treated with zinc chloride (unwashed),
..... treated with zinc chloride (washed).

RATES AND MECHANISMS OF REACTIONS BETWEEN COTTON AND N-METHYLOLATED COMPOUNDS

[SUMMARY]

by

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(Presented by Ralph J. Berni)

Reactions between cotton cellulose and the following finishing reagents in the temperature range between 45° C and 160° C have been studied: dimethylolethyleneurea (DMEU), dimethylolpropyleneureas (DMPU), dihydroxyethyleneurea (DHEU), dimethyloldihydroxyethyleneurea (DMDHEU), and dimethyldihydroxyethyleneurea (DMeDHEU).

All reagents were synthesized in the laboratory, recrystallized, and characterized before use.

Specific reaction rate constants at each of three temperatures for the reactions of cotton with 0.55 M aqueous solutions of the finishing reagent in the presence of 0.03 M Lewis acid catalyst have been determined. From the variations of these rate constants with temperature of reaction, anthalpies, entropies, and free energies of activation have been calculated and compared. Such values obtained under like experimental conditions indicate that reaction mechanisms vary with the structure of the urea moiety in the N-methylolated urea derivatives. For example, data show that although speeds of the cellulose-DMEU and the cellulose-DMPU reactions are about equivalent, the mechanisms of the reactions differ. The large negative entropy of activation of the cellulose-DMEU reaction indicated an S_N2 mechanism, whereas an S_N1 mechanism was indicated for the cellulose reactions with DHEU and DMDHEU. The entropy of activation for the cellulose-DMPU reaction was approximately zero. The order of relative rates of reaction with a given catalyst have been established as follows: DMEU $\cong$ DMPU > DMDHEU > DHEU $\gtrsim$ DMDHEU. With every finishing reagent, the rate of the cellulose modification reaction was greatest with $Zn(NO_3)_2$ catalyst.

Because of the observation that the cation of the inorganic salt used as catalyst was always found in the cellulose products, finished at high temperatures of cure, a study of the metal-ion urea complexes was made. Thus far, the metal ion complexes of cyclic ethyleneurea (CEU) and of cyclic propyleneurea (CPU) have been synthesized and characterized. It has been shown experimentally that the type of ligand ⟶ metal ion bonding differs in going from CEU to CPU with a given metallic ion; and the type of bonding with a given urea differs as the size of the cation is varied. Shifts in infrared bands characteristic of (O-C-N) vibrations in ureas observed in presence of Lewis acids have been explained in terms of stabilization of a resonance hybrid. (Metal ion complexes of these dimethylolated ureas and of the dihydroxy ureas have yet to be isolated and characterized.)

Fabric properties of the finished cottons have been compared. Infrared spectra and micrographs of the finished cottons have also been studied. In finished products, infrared spectra showed that the type of bonding between the urea derivative and Lewis acid differed in products finished with DMEU from those finished with DMPU. Shifts in characteristic bands indicated N as the donor in DMEU resins and O as the donor in DMPU resins. Attempts have been made to correlate these observed differences in finished produces with differences observed in the infrared and NMR spectra of the pure finishing reagents.

Preliminary rate data obtained with catalyst systems consisting of hydrogen ions and metal ions have shown that, while the cellulose reactions are all hydrogen ion catalyzed, the metal ion also catalyzes the cellulose finishing reaction. Selected mixed catalyst systems at constant molarity with respect to total Lewis acid have greater effects on cellulose rate reactions than either acid used alone at like molarity.

DISCUSSION

QUESTION: Is there some relationship between the work with mixed catalyst systems and hydrolysis rates as given by Dr. Vail?

DR. R.J. BERNI: We haven't done this, but it would be interesting to do in light of Dr. Vail's results.

QUESTION: Doesn't Δ F* (free energy of activation) differences imply differences in products rather than differences in mechanism?

DR. R.J. BERNI: Activation parameters, particularly large differences in Δ S* (entropy of activation) — from large negative to zero to large positive values — indicate differences in order of transition state complexes and, hence, in mechanisms.

QUESTION: Since Δ S* is important, is there any comparable data on simple etherification reactions such as with simple alcohols rather than with complex cellulose molecules?

DR. R.J. BERNI: Cellulose behaves differently than simple alcohols and, hence, we did not work on simple compounds since it would not have proved beneficial.

QUESTION: Was 3 minutes at 160° C. sufficient curing time for the slow DMDHEU reaction? Did we actually identify metal ions in the finished fabric? Why aren't amine-hydrochloride catalysts used with resins commercially? Is there something basic about curing with $Zn(NO_3)_2$ or $MgCl_2$ which differs from catalysis with amine-hydrochloride? Is there any evidence that all reactions between N-methylol compounds and cellulose proceeds through monomeric crosslinks, or is there evidence for polymerization? Wasn't the use of pH's as shown a bit low for permanent press processes?

DR. R.J. BERNI: The curing time was sufficient and we did actually find metal in the finished fabric by X-ray fluorescence. Since we did not use the commercial products, I cannot comment on their use with commercial resins. Work of Frick and others showed average crosslinks per anhydroglucose units to be 1.5 indicating a minimum of polymeric crosslinks. The use of pH's as shown on the slide would be low for permanent press, but these were rate studies, and hence, are not being proposed for permanent press processes.

REVERSIBLE CREASE FORMATION IN COTTON CELLULOSE DICYCLOPENTADIENEDICARBOXYLATE FABRICS

by

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New Orleans, La.

(Presented by William E. Franklin)

ABSTRACT

Cotton cellulose fabric was reacted with dicyclopentadienedicarboxylic acid and with dicyclopentadienemonocarboxylic acid in the presence of trifluoroacetic anhydride. The fabric cross-linked with dicyclopentadienedicarboxylic acid had wrinkle recovery angles of 223° (wet) and 191° (conditioned). The wet and conditioned wrinkle recovery angles increased to 274° and 264° when the fabric was heated. Sharp creases were obtained when the fabric was held in a folded position and heated at 145° to 160° C. for 15 minutes or more. These creases were durable to ironing, but could be removed by heating the fabric for extended periods while it was held in a flat position. This reversible crease formation is believed to result from the reversible dissociation and rearrangement of the cross-links at high temperatures. When cotton cellulose dicyclopentadienemonocarboxylate fabric was heated at 160° C. for 2 hours, it developed high wrinkle recovery and retained sharp creases as a result of the dissociation of the substituent groups and the recombination of the cyclopentadienecarboxylate groups remaining on the cellulose.

INTRODUCTION

The presently used durable press and wash-wear finishes for cotton fabrics depend upon covalent cross-links to prevent the formation of wrinkles or undesirable creases in the garment as it is washed or worn. Permanent creases are introduced into garments by chemical reactions which form covalent cross-links as the garment is held in the desired creased configuration. The covalent cross-links, however, make it impossible to remove permanently set creases or to introduce new creases into the garment when alterations or other changes are desired. A cotton finish based on cross-links which could be easily broken and reformed in a new configuration would combine the advantages of the present cellulose cross-linking processes with the property of facile introduction and removal of durable creases.

A number of investigations of potentially reversible cross-linking agents have been reported. Systems involving the breaking of disulfide cross-links by reducing agents and reformation of the crosslinks by oxidation have been reported by Schwenker (16, 17), Mack (12), Hobart (10), Rath (13), and Tesoro (19). Hobart (9) reported an investigation of the reversibility of N-methylolacrylamide cross-links in cotton cellulose in the presence of acidic and basic catalysts.

The above reversible cross-linking systems have the disadvantage that they require treatments with chemical reagents and conditions which are not available to the vendor or user of the treated garments. A cross-linking system which exists as the covalent cross link at ordinary temperatures but dissociates reversibly at high temperatures would have obvious advantages over a system requiring chemical reagents for the dissociation and re-association of the cross-links. Rowland and Brannan (14) have reported a system of divinyl sulfone cross-links in cotton cellulose which also contains covalently attached basic catalytic groups. Mack and Hobart (11) have reported the thermal reversibility of the reaction between cotton cellulose and aryl isocyanates. Rowland and Brannan (15) have investigated the mobility of cross-links in cotton cellulose polycarboxylates.

The thermal reversibility of the Diels-Alder reaction is well known. An example of this thermal reversibility is the cyclopentadiene—dichloropentadiene system, which dissociates to the monomer at elevated temperatures and

reverts to the dimer at lower temperatures. It was believed that a cellulose cross-link containing the dicyclopentadiene structure would provide the basis for an exploratory study of reversible cross-linking in cotton cellulose. Dicyclopentadienedicarboxylic acid has a reactive group attached to each cyclopentadienyl residue in the dicyclopentadiene ring system and could, therefore, serve as a thermally reversible cross-linking agent. Dicyclopentadienedicarboxylate cross-links would be preferred to other cross-links dissociating by the reverse Diels-Alder reaction because each cyclopentadienecarboxylate group produced in the dissociation could serve as either the diene or the dienophile in the re-association.

The thermal dissociation of dimethyl dicyclopentadienedicarboxylate in the presence of trapping agents had been reported (5), and the kinetics of the dissociation have been measured (6). The kinetics of the reverse Diels-Alder dissociations of cellulose dicyclopentadienemonocarboxylate groups in swollen and in collapsed cotton fibers have been investigated (7). The present report describes the effects of these reversible cross-links on the wrinkle recovery properties of the fabric and the extent to which durable creases may be introduced and removed in these cross-linked cotton cellulose fabrics.

EXPERIMENTAL

Materials.—The fabric employed in this study was 80 x 80 desized, scoured, and bleached cotton printcloth weighing approximately 3.2 oz./yd. Trifluoroacetic anhydride (TFAA), from Peninsular ChemResearch, Inc., and maleimide, from Aldrich Chemical Company, Inc., were used without further purification. Dicyclopentadienedicarboxylic acid (tricyclo]5,2,1,$0^{2,6}$]deca-3, 8-diene-4,9-dicarboxylic acid, DCD) was obtained from K&K Laboratories and recrystallized to a constant melting point of 209° to 211° C. before use.

A mixture of isomeric dicyclopentadienedicarboxylic acids was prepared as previously reported (5) and contained approximately equal amounts of tricyclo]5,2,1,$0^{2,6}$]deca-3, 8-diene-1,4-dicarboxylic acid and the 4,9-dicarboxylic acid.

Test methods. — Nitrogen analyses were carried out by Galbraith Laboratories, Inc. Conditioned and wet wrinkle recovery angles were measured by the Monsanto method (1). Crease ratings were measured by a modification of the AATCC method described by Hobart (9). Crease retention angles (CRA) were measured by a modification of the Goldstein method reported by Blanchard and others (2). Further modifications for use with printcloth were as follows: A 5.0 g. weight was placed in the center of the horizontal leg to assure a flat horizontal surface. The time of relaxation was reduced to 5 min., since the measured CRA changed less than 1° in the following 24 hrs. Each CRA measurement was done in triplicate, and the averages are reported. The range of values was generally less than ±3°, with occasional ranges up to ±7°.

Saponification equivalents were evaluated by hydrolysis with sodium hydroxide (18). Free carboxylic acid groups were measured by reaction with silver o-nitrophenolate, followed by potentiometric titration of the excess silver with hydrochloric acid (4). The analytical results are reported in terms of ester groups per anhydroglucose unit and free carboxylic acid groups per anhydroglucose unit.

Esterification reactions. — The cotton cellulose esters were prepared by the trifluoroacetic anhydride (TFAA) method (3, 8). The reaction of cotton cellulose with dicyclopentadienemonocarboxylic acid (DCM) has been described (7). In a typical preparation of cotton cellulose dicyclopentadienedicarboxylate, cotton fabric (9.91 g., 0.061 mole of anhydroglucose units) was swollen in hot water and solvent exchanged four times each with anhydrous methanol and anhydrous benzene. The fabric was rolled with loosely woven fiberglass cloth and immersed in a solution prepared from 3.30 g. (0.015 mole) of the mixed isomers of DCD, 10.4 ml. (15.6 g., 0.074 mole) of TFAA, and 100 ml. of anhydrous benzene and contained in a glass tube. The tube was sealed, thoroughly shaken, and maintained at room temperature for 24 hrs. with occasional shaking. The fabric was washed with benzene, acetone, methanol, and water. A further treatment with boiling methanol was necessary to remove the remaining trifluoroacetate groups from the fabric. The dried fabric weighed 10.63

g., (7.3 percent add-on). The fabric was ironed at a hot cotton setting (204° C.).

Reaction of cellulose dicyclopentadienedicarboxylate with maleimide. — Cotton cellulose cross-linked with DCD (Fabric 1, table 1, unironed, 0.333 g.) was placed in a solution of 0.27 g. of maleimide in 75 ml. of xylene, and the solution was heated overnight at reflux. After the fabric was thoroughly washed in benzene, acetone, alcohol, and water and dried, it weighed 0.344 g. (3.6 percent add-on). The fabric contained 1.13 percent nitrogen. The conditioned wrinkle recovery angle decreased from 191° to 125° (W+F).

When a sample of the same crosslinked cellulose fabric which had been ironed at a hot cotton setting (204° C., 2 minute total time) was treated with maleimide in the same manner, it showed a 3.8 percent add-on and a nitrogen content of 0.62 percent. The conditioned wrinkle recovery angle of this sample decreased from 263° to 217° (W+F). Unmodified cotton fabric subjected to the maleimide treatment showed a 1.3-percent weight loss and a nitrogen of 0.37 percent after the treatment. The conditioned wrinkle recovery angle of the unmodified fabric changed from 165° to 139° (W+F).

Introduction of durable creases. — Creases were introduced into cotton fabrics by folding 4 x 6 cm. pieces of the fabric along the length so that the warp yarns were creased. The folded fabric was clamped between glass plates and the assembly was heated in the oven for the desired time and temperature. In one series of experiments, the fabric samples were heated in refluxing diglyme (b.p. 160° C.). The samples were removed from the oven and cooled. The fabric was removed from the glass plates and agitated with hot (60° C.) water for 1 hour. The samples were spread open and allowed to dry. Samples for measurements of CRA (1.5 cm. wide, 1 cm. on each side of the crease) were cut from the fabric. The samples were wetted with distilled water and allowed to dry and equilibrate at a relative humidity of 65 percent for at least 16 hours while spread open with the crease side up.

After the CRA measurements were made, the samples were ironed flat (10 sec. with steam, 20 sec. without steam, 145° C) with the crease side up. After equilibration, the CRA was again measured to find the durable crease remaining in the fabric.

RESULTS AND DISCUSSIONS

The esterification procedure was similar to that used by Campbell and Francis (3) in the concentrations of reagents used, but the reaction times were two to three times those used by Campbell and Francis. Table 1 shows the mole ratios of reactants and the analyses of the fabrics. The extent of diester formation in the reactions of cotton cellulose with dicyclopentadienedicarboxylic acid (DCD) was similar to those reported by Campbell and Francis for the esterification with dodecanedioic acid, but the acid number and the ratio of monoester to diester were higher than those reported by Campbell and Francis. The higher ratio of monoester to diester can probably be ascribed to the fact that the DCD molecule is quite rigid and bulky between the reactive groups. The DCD cross-links might, therefore, be expected to show spatial restrictions not shown by the more flexible straight-chain dicarboxylate cross-links.

The treatment of the fabrics with water before the solvent exchanges and the presence of free trifluoroacetic acid (from the acid-anhydride equilibrium) in the esterification solution caused the cotton fabrics to be highly swollen as the esterification was carried out. The expected higher wet wrinkle recovery angle (WRA) than dry WRA was observed in the adipate cross-linked fabric and in two of the DCD cross-linked fabrics before ironing, as seen in table 2. When the fabrics 1 and 2 (table 1) were ironed at a cotton-linen setting (204° C, four times, 30 sec. each), both the wet and dry WRA's increased to approximately the same values. These two fabrics were not treated with hot methanol before the WRA's were measured. Fabrics 3 and 4 (table 1) were heated in methanol at 60° to 65° for 1 hour in order to remove the trifluoroacetate groups remaining after the previous washings before the WRA's were measured. These last two fabrics had high wet and dry WRA's and showed only slight changes in WRA when the fabrics were ironed.

These changes in WRA caused by heating are those to be expected in fabrics containing cross-linking groups which are capable of dissociating when heated. When the fabric is washed after the reaction and allowed to dry, the cellulose matrix will tend to collapse, but the cross-links will remain in positions appropriate for the swollen cellulose matrix. As the fabric is heated, either by ironing or in hot

Table 1. — Reaction of cotton fabrics with carboxylic acids and TFAA

Fabric No.	Acid	Mole ratio acid/TFAA/AGU	Time, days	Pct. weight increase	Sapon. equiv./AGU	Free COOH	Crosslinks per AGU
1	DCD[1]	0.015/0.037/0.035	2	9.6	——	——	——
2	DCD[2]	.015/.037/.042	4	6.5	0.096	0.028	0.020
3	DCD[2]	.015/.074/.061	3	7.3	.113	.036	.021
4	DCD[2]	.030/.120/.110	1	6.6	.124	.037	.025
5	DCM[3]	.021/.042/.042	2.5	36.4	.42	——	——
6	Adipic	.030/.120/.110	1	7.0	——	——	——
7	Benzoic	.060/.120/.110	1	3.4	——	——	——

[1] DCD, dicyclopentadienedicarboxylic acid (4, 9-dicarboxy isomer).

[2] Dicyclopentadienedicarboxylic acid, mixture of 1, 4- and 4, 9-dicarboxy isomers.

[3] DCM, dicyclopentadienemonocarboxylic acid (4-carboxy isomer).

Table 2. — Wrinkle recovery angles of esterified fabrics

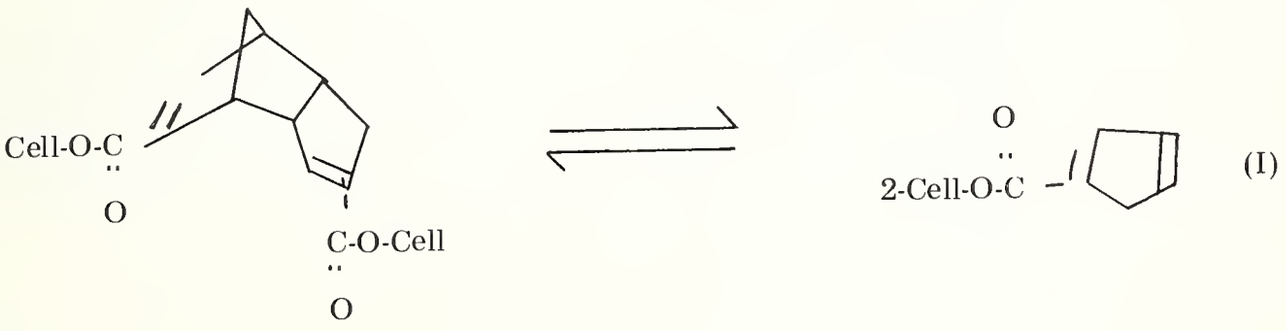
		Wrinkle recovery angles (W+F, deg.)			
		Before ironing		After ironing	
Fabric No.	Acid	Conditioned	Wet	Conditioned	Wet
1	DCD	191	223	264[1]	274[1]
2	DCD	237	256	264	259
3	DCD	288[1,2]	264[1,2]	268[1]	270[1]
4	DCD	278[1,2]	272[1,2]	276[1,3]	274[1,3]
5	DCM	188[1]	164[1]	248[1,3]	254[1,3]
6	Adipic	224	270	231	280
7	Benzoic	149	167	179	177
8	None	165	160	193	168

[1] 2 X W.

[2] After heating in methanol at 65° for 1 hour.

[3] Heated 2 hr. at 160°.

methanol, the dicyclopentadienyl groups in the cross-links reversibly dissociate by the reverse and forward Diels-Alder reactions. These reactions may be represented by the following equation, where Cell-O-represents the cellulose chains to which the DCD groups are bonded:



(I)

When cross-links break by this reaction, the cellulose chains are free to move toward more favorable positions in the collapsed matrix. Cross-links originating from different DCD molecules are formed in new positions in the collapsed fibers. The fabric thus develops increased dry wrinkle recovery as a result of the heating.

The kinetics of the dissociations of the dimethyl ester of DCD (6) and the cellulose ester of dicyclopentadienemonocarboxylic acid (DCM) (7) would seem to indicate that 2 hours would be insufficient time for a significant amount of dissociation to occur in methanol at 65°. The tendency of the cotton cellulose matrix to collapse would introduce strain in the DCD cross-links similar to that observed in the DCM ester groups in collapsed cotton cellulose (7); therefore, the energy of activation of the dissociations of the DCD cross-links would be expected to be similar to that found for the dissociation of the DCM ester groups in collapsed cellulose. Since the cellulose chains in the DCD cross-linked fabric would be moving toward a more favorable position in the collapsed cellulose matrix, a restriction of diffusion would not lower the entropy of activation for the dissociation reaction. An antropy of activation close to that found for the dissociation of DCM groups in swollen cotton cellulose fibers would be expected for this rearrangement of DCD cross-links. Combination of the expected activation energy (18.5 kcal) with the expected entropy of activation (zero eu) gives a reasonably fast rate for the dissociation of DCD cross-links changing from the swollen state to the collapsed state at 65° C. The failure of the cellulose adipate fabric to improve the WRA upon heating excludes the possibility of rearrangement of the diester cross-links by transesterification reactions.

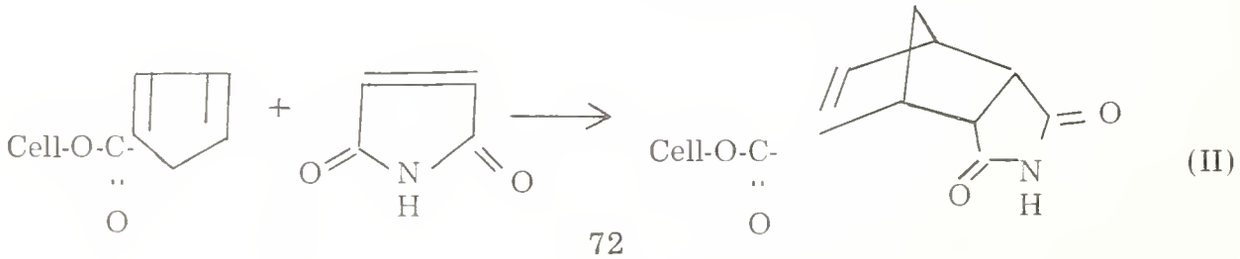
When the DCD cross-linked cotton cellulose fabric was heated in the presence of maleimide, the reversible Diels-Alder dissociation (equation I, above) was intercepted by the Diels Alder reaction of the active dienophile, maleimide, with the cellulose cyclopentadienecarboxylate groups to produce the more stable maleimide adduct:

The add-on and the nitrogen analyses indicate that maleimide was covalently bonded to the cellulose through the cyclopentadienecarboxylate groups. The lower WRA's of the fabrics after reaction with maleimide indicate that the DCD cross-links were irreversibly broken by the process.

Attempts to introduce durable creases into DCD cross-linked cotton fabrics by ironing for 30 seconds at a cotton-linen setting (204° C.) in the presence or absence of nonvolatile potential swelling agents developed no more durable creases than those obtained from similar treatments of unmodified control fabrics.

Since it has been found that the reverse Diels-Alder dissociation of the dimethyl ester of DCD had a half-life of approximately 7.5 minutes at 140°, it was believed that longer periods of heating might be required to introduce durable creases into the DCD cross-linked fabrics. Accordingly, samples of the cross-linked fabric were constrained in a creased configuration by clamping them between glass plates. The assembly with the folded fabric was heated in the oven for 2 hours at 160° C. The durability of the creases in the fabric samples was measured by washing them in hot water for 2 hours (step I). Since both the cross-linked and the control fabrics retained sharp creases after the washing, the fabric samples were spread open and ironed flat (step II) in order to remove nondurable creasing. Crease retention angles (CRA) were measured after both steps. Cotton cellulose fabrics esterified with DCM, adipic, and benzoic acids were also subjected to the same treatment. Table 3 gives the crease retention angles (CRA) of these fabrics after step II of the crease durability test. The DCD and DCM esterified fabrics retained sharp (low CRA) creases after ironing, while the adipate and unmodified fabrics retained almost no crease (CRA close to 180°).

The durable creasing in the DCD fabric results from the rearrangement of existing cross-links, while that in the DCM fabric results from the formation of DCD cross-links between cellulose



(II)

Table 3. — Durable creases in esterified cellulose fabrics heated 2 hours at 160°

Fabric No.	Acid	CRA[1] (deg, after step II[2])
4	DCD	99
5	DCM	109
6	Adipic	169
7	Benzoic	149
	None	168

[1] CRA: Crease retention angles, values from 180° (no crease) to 0° (perfect crease).

[2] Step II of crease durability test: fabric spread open and ironed flat.

cyclopentadienecarboxylate groups, which result from the dissociation of DCM groups during the heating period. The loss of weight by the DCM fabric on heating (7) corresponds to that calculated for the loss of one molecule of cyclopentadiene from each substituent group. The failure of the adipate fabric to form durable creases excludes the possibility of rearrangement of cross-links by transesterification reactions, while the poor durable creasing of the benzoate fabric indicates that durable creasing by plasticization of the cellulose by ester groups is of minor importance in this system.

The effect of time of heating on the durable creasing process is seen in table 4. The CRA's after steps I and II of the crease durability test are given both for the DCD cross-linked fabric and for the unmodified control fabric after various periods of heating. Sharp creases are rapidly formed in the unmodified fabric and not removed from the small fabric samples by washing, but the creases are almost completely removed by ironing the unmodified cotton samples. In contrast, the DCD cross-linked fabric attained a sharp crease more slowly at 160° C., but most of the crease was retained after ironing. The ultimate crease sharpness in the cross-linked fabrics, both before and after ironing, was attained after approximately 75 minutes of heating. The fabric samples heated at 160° C. for 120 minutes or more showed considerable discoloration. Those heated at this temperature for 180 minutes were extremely brittle.

Table 4. — Durable crease formation at 160°

	Crease retention angles (deg.)			
	Fabric No. 4, DCD		Unmodified control	
Time (min.)	After step I[1]	After step II	After step I	After step II
15	123	148	113	168
30	113	136	105	166
45	110	134	---	---
60	105	143	116	168
75	97	126	---	---
90	82	110	111	170
120	96	119	105	169
150	96	120	---	---
180	96	115	111	173

[1] Step I of crease durability test: washing in hot water for 2 hr.

The formation of durable creases in DCD cross-linked fabrics at 145° C., as seen in table 5, shows the same effects seen at 160° C. The

Table 5. — Durable crease formation at 145°

	Crease retention angles (deg.)			
	Fabric No. 2 (DCD)		Unmodified control	
Time (min.)	After step I	After step II	After step I	After step II
16	157	161	141	170
31	138	152	144	168
62	135	145	136	165
180	110	130	138	167

initial formation of sharp creases in the cross-linked fabric is slower than in the unmodified fabric. When the creases are formed in the cross-linked fabric, they are sharper than those in the unmodified fabric, and they are durable with respect to ironing. As would be expected for a chemical reaction, the rate of dissociation and rearrangement of the cross-links and, therefore, the rate of crease formation is slower at the lower temperature.

The reversibility of durable crease formation is shown in table 6, which gives the CRA's (after

Table 6. — Reversibility of crease formation

	Fabric No. 3, Temperature 160°			
	Crease formation		Crease removal	
Sample	Time (min.)	CRA, deg. (After step II)	Time (min.)	CRA, deg. (After step II)
1	15	147	150	173
2	30	135	150	170
3	61	119	150	166
4	90	116	150	165
5	120	111	150	165

step II) produced by heating another DCD cross-linked fabric for various periods at 160° C., and the CRA's after an uncreasing operation. The creased fabric samples were uncreased by clamping them open between glass plates and heating at 160° C. for 2-1/2 hours. The CRA's of the uncreased samples were measured after step I; the differences of these values from 180° indicate that the fabrics were not completely smooth after washing, rather than that any crease remained in the fabric.

It is to be expected that the rearrangement of the cellulose matrix in the formation of a durable crease will involve less relief of internal strain than the rearrangement of the cellulose matrix from the swollen state to the collapsed state. The smaller driving force in the formation of a durable crease is reflected in the slow rate of durable crease formation. The difference between the apparent rate of crease formation and the rates of dissociation of the dimethyl ester of DCD (6) and the cellulose ester of DCM (7) indicates that another effect enters into the formation of durable creases by the dissociation and rearrangement of DCD cross-links. A requirement that a number of cross-links be dissociated at the same time to permit the movement of a section of the cellulose chain may be such an effect.

SUMMARY

Cotton cellulose fabric has been cross-linked with dicyclopentadienedicarboxylic acid, using trifluoroacetic anhydride as impeller. The cross-linked fabric had low wet and conditioned wrinkle recovery angles. When the fabric was heated, the wet and conditioned wrinkle recovery angles both increased to 260° to 270° (W+F). The thermal dissociation of the dicyclopentadienedicarboxylate cross-links was shown by the reaction of the cross-linked fabric with maleimide, which decreased the wrinkle recovery angle and caused an increase in weight and nitrogen content of the fabric. Although it was not possible to durably crease the fabric by ironing, durable creases could be formed in the fabric by heating the folded fabric at 145° or 160° for 15 minutes or more as it was being held between flat plates. The creases formed by this process were durable to washing and ironing, but they could be removed by heating the fabric as it was being held open between flat plates. The formation and removal of these durable creases is believed to result from the reversible dissociation and rearrangement of the dicyclopentadienedicarboxylate cross-links at high temperatures.

Cotton cellulose fabric was reacted with dicyclopentadienemonocarboxylic acid in the presence of trifluoroacetic anhydride. The esterified cellulose fabric had a conditioned wrinkle recovery angle of 188°. When the esterified cellulose fabric was heated at 160° for two hours, the substituent groups dissociated and the cyclopentadienecarboxylate groups remaining in the cellulose dimerized to form dicyclopentadienedicarboxylate cross-links, increasing the conditioned wrinkle recovery angle to 248°. If the fabric was folded during the heating period, the creases were durably set in the cross-linked fabric.

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Textile Testing Group for measuring the wrinkle recovery angles and for their advice on the measurement of crease retention angles.

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DISCUSSION

QUESTION: You stated that there were two cross-links per 100 anhydroglucose units in cotton cross-linked with dicyclopentadiene decarboxylic acid. How many are there after the cross-links have been broken and reformed?

DR. W.E. FRANKLIN: The initial measurement was made on fabric that had already been heated. The fabrics were ironed before the titrations.

QUESTION: Do you have any data of strength retention? Doesn't trifluoroacetic anhydride degrade cotton?

DR. W. E. FRANKLIN: Yes, trifluoroacetic anhydride degrades cotton. We observed a 33-percent decrease in breaking strength of fabrics treated with trifluoroacetic anhydride in the absence of other reagents.

QUESTION: Is this relative to unmodified cotton?

DR. W.E. FRANKLIN: Yes.

QUESTION: Could you use active esters rather than the trifluoroacetic anhydride technique?

DR. W.E. FRANKLIN: Yes, but this is really only a pilot study. In actual practice one would not use ester linkages at all since they would wash out quite easily. The trifluoroacetic acid residues hydrolyze off and are measured as free carboxyl groups, while residues from other activating reagents would not wash out as easily.

QUESTION: Have you tried non-aqueous solvents? Can you do away with the water?

DR. W.E. FRANKLIN: Yes, this is a non-aqueous system.

FREE RADICAL REACTIONS BETWEEN HYDROGEN PEROXIDE AND COTTON CELLULOSE INITIATED BY LIGHT AND/OR METAL IONS

[SUMMARY]

by

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New Orleans, La.

(Presented by Oscar Hinojosa)

Reactions between hydrogen peroxide and cotton cellulose have been used to initiate graft copolymerization reactions of vinyl monomers with cellulose. It has been suggested that such reactions initiated by light or metal ions or both involve free radical processes. Direct experimental evidence of the proposed free radicals was not possible before the introduction of electron spin resonance spectroscopy.

Using ESR spectroscopy the spectra for free radicals produced by reactions involving cotton cellulose and cotton cellulose with hydrogen peroxide using various methods of initiation have been determined. When purified cotton cellulose was placed in the cavity of the spectrometer and irradiated at room temperature with ultraviolet light from a high intensity mercury vapor lamp, an ESR spectrum was generated. The spectrum generated was a singlet with line width of about 8 to 10 gauss. The intensity of the signal increased with time of irradiation and leveled off after about 30 minutes.

When hydrogen peroxide was used, the reactions were carried out at low temperature to minimize absorption of microwave power by the aqueous solutions. A singlet spectrum was generated upon irradiation of the cotton cellulose which had been immersed in hydrogen peroxide solution (0.1 M) before cooling to -100° C. This signal was more intense than the signal produced upon irradiation of the dry cotton cellulose.

Irradiation of cotton cellulose immersed in ferrous sulfate solution (0.01 M) without added hydrogen peroxide again generated a singlet spectrum. However, this signal was more intense than either the signal generated on dry cotton or the signal generated on the cellulose/hydrogen peroxide system. In both of the aqueous systems, the intensity of the signal depended on the pH of the solutions used and upon the temperature of the sample at the time of irradiation.

The crystallinity of the cellulose also had an effect on the intensity of the free radical spectra generated in these systems. The intensity of the signal was greater in decrystallized cellulose than in cellulose I. This effect suggests that the free radical formation takes place mainly in the amorphous regions of the cellulose, probably because the reagents can easily penetrate into the less ordered areas of the cellulose.

Reactions between hydrogen peroxide and cotton cellulose initiated by ferrous ion alone required a more complicated technique for the determination of the ESR spectra of the free radicals involved. Although hydroxyl radicals, generated by the Fe^{2+}/H_2O_2 system, were not observed directly, they were shown to abstract hydrogen atoms from sorbitol and cellobiose. The ESR spectra of cellobiose and sorbitol radicals generated by the Fe^{2+}/H_2O_2 system were observed by using an aqueous flow cell at 25° C. In the case of the fibrous cotton cellulose, the cellulose was first immersed in 0.1 M $FeSO_4$ solution and then dried in a flowing stream of nitrogen. Then the dried cellulose, containing $FeSO_4$, was wet with 0.3 M H_2O_2 and immediately frozen in liquid nitrogen. The spectrum was recorded at -110° C. and consisted of a three-line spectrum. The structure of this spectrum suggests that the free radical was formed by abstraction of hydrogen from the hydroxyl group at carbon C_6.

When the hydrogen peroxide was saturated with acrylonitrile monomer and then applied to the dry cellulose containing $FeSO_4$, an ESR

spectrum was generated which differed from the ESR spectrum generated in the absence of monomer. This ESR spectrum, generated in cellulose during the copolymerization reaction was several times more intense than the ESR spectrum generated in cellulose by the Fe^{2+}/H_2O_2 system. The spectrum appeared to be a combination of two strong singlet spectra, one with $\Delta H = 15$ gauss and the other with ΔH = about 62 gauss. One of the singlet spectra was likely generated on carbon C_1 or C_4 on depolymerization of the cellulose molecule, and the other was probably generated on the end of the growing polyacrylonitrile molecular chain. The ESR spectrum generated on microcrystalline cellulose during the copolymerization reaction was less intense than that generated on cellulose I, probably due to the greater crystallinity of the microcrystalline cellulose.

DISCUSSION

QUESTION: What practical applications do the results of these types of investigations have?

MR. O. HINOJOSA: The generation of highly reactive hydroxyl and perhydroxyl radicals can lead to the oxidative degradation of cotton cellulose through free radical processes. The control and useful application of new knowledge, developed in these investigations, can be applied in the following ways: (1) Weathering degradation — when cotton products are contaminated by the presence of metal ions, such as ferric, ferrous, ceric, and titanic, the generation of hydrogen peroxide by the interaction of sunlight with water and then generation of the reactive radicals on the reaction of hydrogen peroxide with any of the metal ions listed can accelerate the degradation and loss in strength of the cotton products. (2) Graft copolymerization — under controlled conditions, the generation of reactive radicals on reaction of hydrogen peroxide with these metal ions leads to the abstraction of hydrogen atoms from the cellulose molecule to form free radical sites where graft copolymerization with vinyl monomers can be initialed to change the textile properties of cotton. (3) Bleaching cotton products with peroxides — similarly the generation of reactive radicals in reactions as outlined in (1) and (2) must be minimized to decrease degradation and loss in strength of cotton during bleaching reactions.

QUESTION: Have chemical methods, in addition to ESR, been used to identify the location of free radical sites on the cellulose molecule?

MR. O. HINOJOSA: No. However, ESR spectra depend on the chemical structures involved and identification of free radical sites on cellulose is relatively certain.

FIBROUS CHLOROCELLULOSE YARN: ITS PREPARATION, PROPERTIES AND REACTION WITH NUCLEOPHILIC SULFUR AND NITROGEN COMPOUNDS

by

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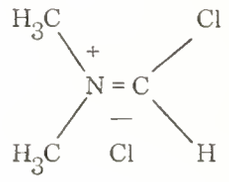
ABSTRACT

Fibrous chlorodeoxycellulose with a D.S. as high as 0.3 can be prepared by reacting alkali-activated cotton yarns with thionyl chloride in dimethylformamide at room temperature. The resultant yarns possess the same tensile strength as untreated yarn, and exhibit increased rot resistance. The chlorocellulose yarns can be converted into new fibrous cellulose thioethers, such as carboxymethylthiocellulose (Cell-S-CH_2-COOH). The yarns also can be converted into cross-linked diaminodeoxycelluloses by reaction with primary aliphatic diamines.

INTRODUCTION

The preparation of chlorodeoxycellulose (hereafter called chlorocellulose) in fibrous form is important since it affords a cellulosic textile material having different functional group chemistry than native cotton. The first reported preparations of chlorocellulose were accomplished by the reaction of cotton linters with pyridine and thionyl chloride (2, 3), but the cellulose was degraded and lost its fibrous structure by such a treatment. Fumasoni and Schippa (5) prepared chlorocellulose by reacting high purity filter paper with thionyl chloride in chloroform or carbon tetrachloride with iron as a catalyst. Polyakov and Rogovin (7) were successful in preparing chlorocellulose without apparent degradation by reacting activated cotton linters with thionyl chloride in dimethylformamide at 60° to 98° C. The lack of degradation was attributed to the fact that dimethylformamide ties up the liberated hydrochloric acid as the formiminium salt,



We wish to report some of the textile and chemical properties of chlorocellulose yarns prepared by the method of Polyakov and Rogovin (7). An important modification of their procedure is that the reaction was conducted at room temperature. When elevated temperature was used, yellowing and disintegration of the yarns occurred. The effect of time and thionyl chloride concentration on the chlorine content, rot resistance, and tensile properties are discussed. Also, the preparation of new cellulose derivatives from chlorocellulose are described, including the preparation of cellulose thioethers and diaminodeoxycelluloses.

EXPERIMENTAL

Materials. — The source of cellulose was Deltapine 21/3, loose-twist, kiered cotton yarn.

The thionyl chloride, dimethylformamide, the mercaptoacids, and the primary aliphatic diamines were commercial reagent grade.

Yarn treatments. — The yarn was activated for chlorination by the following sequence: (a) Immersing in 23 percent sodium hydroxide for an hour at 25° C., (b) washing with tap water until all alkali was removed, (c) immersing in 95 percent ethanol for 24 hours, and (d) immersing and storing in benzene for 24 to 96 hours.

The chlorination process consisted of squeezing out excess benzene from the activated yarn, immersing the yarn in dimethylformamide, and then adding thionyl chloride dropwise to maintain the solution at room temperature. The bath ratio was 40 g. of dimethylformamide-thionyl chloride to 1 g. of cotton yarn. Reaction times listed were computed after addition of all the thionyl chloride. The yarns were then washed with ice water until most of the thionyl chloride was removed. They were then immersed in 3 percent ammonium hydroxide for an hour, tap-water washed, washed with acetone, and air-dried.

Chlorocellulose yarns were reacted with mercaptoacids by first converting the mercaptoacid to its completely anionic form (addition of two equivalents of potassium hydroxide per mole of monocarboxylic mercaptoacid, or three equivalents in the case of 2-mercaptosuccinic acid) in 50 percent ethanol-50 percent water, then immersing the chlorinated yarn in these solutions for an hour at 60°, 80°, and 100° C. The ratio used for these reactions was one gram of chlorocellulose per 0.02 mole of mercaptoacid. Excess mercaptoacid was removed by boiling the yarn for 30 minutes in 95 percent ethanol. The samples were then washed with water and air-dried.

Chlorocellulose yarns were reacted with amines by immersion for 24 hours at 105° in 10- and 50-percent n-butanol solutions containing the amine. The yarns were subsequently washed with 95 percent ethanol, then water, and air-dried.

Analyses and tests. — The breaking strength and elongation-at-break values of the yarns were determined by ASTM D-2256-64T. The energy-to-rupture measurements were determined by means of an automatic integrator attached to an Istron tester. Yarns were tested for rot resistance by the soil burial method AATCC 30-1957T.

Elemental analyses, corrected for moisture and ash content, were performed by a commercial laboratory.

Cuene solubilities were determined in a manner similar to that described by Frick and others (4). Methylene blue dye tests were conducted as follows: For every 5 g. of cotton, 1 ml. of 0.5 percent methylene blue solution and 49 ml. of distilled water were used; the samples were allowed to boil for 5 minutes, tap-water washed for 20 minutes and allowed to air-dry. Kiton Red dye tests were performed as follows: For every gram of cotton, 5 ml. of 1 percent Kiton Fast Red solution and 45 ml. of distilled water were used; the samples were allowed to boil for 5 minutes, tap-water washed for 20 minutes, and allowed to air-dry.

RESULTS AND DISCUSSION

Preparation of chlorocellulose yarn. — Rogovin (7) was successful in obtaining cellulose with high chlorine content by reacting activated cotton linters with thionyl chloride in dimethylformamide at elevated temperatures. However, we found that when activated yarns were reacted under similar conditions, the cotton was yellowed and degraded when the reaction temperature was raised above 30°. At temperatures of 25° to 30°, we were able to introduce as much as 6.2 percent chlorine into the cotton yarn, giving a D.S. of 0.3, without discoloration or loss of breaking strength.

It was necessary to activate the yarns before reaction to obtain yarns with appreciable chlorine content. This was done by employing Rogovin's procedure (7). If the yarn was simply oven-dried before reaction, the chlorine content was negligible (table 1, sample 7), and the yarn had poor tensile strength.

The effect of reaction time on the chlorine content of the yarns was investigated. If the thionyl chloride concentration were held constant, the chlorine content increased with reaction time. For yarn treated with 10 percent thionyl chloride, the chlorine content rose 2.5-fold when the reaction time was increased from 1 to 4 hours (see table 1). However, at a thionyl chloride concentration of 20 percent, the chlorine content increased by only 40 percent after a similar increase in reaction time.

Table 1. — Effect of reaction time and thionyl chloride concentration on physical and chemical properties of activated kiered yarn

Sample	Reaction time	$SOCl_2$	Breaking strength	Elongation	Tenacity	Energy to rupture	Cl[1]	S	Moisture	Ash
	Hour	Pct.	Lb.	Pct.	G./tex	Lb.	Pct.	Pct.	Pct.	Pct.
1	1	10	6.1	23.4	14.2	4.4	1.6	trace	7.5	0.1
2	4	10	5.5	24.4	13.2	3.9	4.3	trace	6.9	0.1
3	1	20	4.5	23.7	9.8	3.1	4.4	trace	7.7	0.1
4	4	20	5.2	30.9	10.8	4.6	6.2	0.4	8.1	1.0
5	None[2]	--	6.8	28.5	16.3	6.4	---	---	---	---
6	None[3]	--	5.4	10.1	17.8	1.8				
7	4[4]	20	3.4	9.4	10.9	1.0	0.3	trace	---	---

[1] All chlorine and sulfur values are corrected for moisture and ash, except sample 7.
[2] Activated, then water-washed, and air-dried.
[3] Untreated kiered yarn.
[4] Unactivated, but dried for 10 min. at 105° before immersion in dimethylformamide.

The chlorine content increased with increasing thionyl chloride concentration. At a reaction time of 1 hour, the chlorine content increased nearly threefold when the thionyl chloride concentration was raised from 10 to 20 percent. With a longer reaction time (4 hours), the chlorine content changed only 44 percent over this concentration range.

Properties of chlorocellulose yarn. — As shown in table 1, the breaking strength of the chlorinated yarns was 90 to 100 percent of that of untreated kiered yarn. Treated, unactivated yarn (sample 7) had little chlorine content and retained only 63 percent of its breaking strength compared with the untreated kiered yarn.

The chlorocellulose yarns possessed some rot resistance. This resistance was found to be roughly proportional to the percentage of chlorine in the cellulose. Untreated yarn and the yarn with 1.6 percent chlorine disappeared within 2 weeks of burial. After 2 weeks, however, samples with 4 to 6 percent chlorine had breaking strength retentions of 12 to 72 percent. After 4 weeks, the yarns with 4.4 and 4.3 percent chlorine (see table 2) had disappeared, while the yarn with 6.2 percent chlorine had a strength retention of 33 percent. After 6 weeks, the latter sample still had 26-percent strength retention.

Reactions of chlorocellulose yarn - general considerations. — One can envision chlorocellulose being capable of undergoing numerous nucleophilic substitution reactions to produce new and interesting cellulose derivatives. Rogovin (7) was successful in preparing the aminodeoxy- and cyanodeoxy-derivatives from chlorocellulose linters. Yuldashev (10, 11) succeeded in phosphorylating cellulose by the reaction of chlorocellulose with phosphoric acid esters. We investigated the interaction of chlorocellulose yarns with a number of nucleophiles, and found thioacids and primary diamines among the most reactive. Certain of these nucleophiles were cross-linking agents for cellulose, and gave yarns with desirable physical properties.

Reaction with thioacids. — Chlorocellulose yarns (4.7 percent Cl) were reacted with aliphatic and aromatic mercaptoacids at various temperatures. The acids used were 2-mercaptoacetic, 3-mercaptopropionic, 4-mercaptobutyric, 2-mercaptosuccinic, and o-mercaptobenzoic. The resultant products represent a new series of cellulose derivatives, the

Table 2. — Rot resistance of chlorocellulose yarns

Cl[1]	2 weeks		4 weeks		6 weeks	
	Breaking strength, lb.		Breaking strength, lb.		Breaking strength, lb.	
	Retained[2]	Elongation	Retained[2]	Elongation	Retained[2]	Elongation
Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
1.6	D[3]	D[3]	---	---	---	---
4.3	1.6(30)	12.3	D[3]	D[3]	---	---
4.4	0.6(12)	7.6	D[3]	D[3]	---	---
6.2	3.7(72)	20.9	1.7(33)	11.8	1.3(26)	15.5
Untreated	D[3]	D[3]	---	---	---	---

1/ Corresponds to samples described in table 1.

2/ Compared with untreated, kiered yarn.

3/ = disappeared.

simplest member being carboxymethylthiocellulose (Cell-S-CH_2-COOH).

Complete nucleophilic displacement of the chlorine was never achieved, even at temperatures of 100°. Usually 60 to 75 percent of the chlorine was displaced by the mercaptoacid. This same trend was observed by Rogovin (7) in his reaction of chlorocellulose linters with potassium cyanide in dimethylformamide.

The extent of cellulose thioether formation was greatly dependent on the reaction temperature at which the chlorocellulose was reacted with the mercaptoacid. For the homologous series HS-$(CH_2)_n$-COOH, and for 2-mercaptosuccinic acid, the optimum reaction temperature was 80°. At this temperature, the resultant cellulose thioethers had sulfur contents of 2.4 to 3.2 percent (see table 3). This represents 60 to 70 percent nucleophilic displacement of the chloro group.

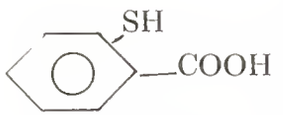
Below 80°, the aliphatic mercaptoacids displaced less than 50 percent of the chlorine; sulfur contents (see table 3) were about half of those obtained by reaction at 80°. Above 80° the sulfur contents obtained by treatment with aliphatic mercaptoacids were somewhat lower than those at 80°, but the chlorine content was also reduced.

With the aromatic mercaptoacid (o-mercaptobenzoic) the optimum reaction temperature was 60°. At this temperature, o-carboxyphenylthiocellulose, containing 3 percent sulfur was obtained. At higher reaction temperature, the resultant yarns contained less sulfur and chlorine.

Most of the mercaptoacid treatments rendered the chlorocellulose at least temporarily insoluble in 0.5 M cupriethylenediamine. A very low degree of cellulose cross-linking appeared to have occurred. The mercaptoacids studied contained but one thiol group per molecule. However, they were applied as their potassium salts, in which form they may have caused appreciable esterification as well as thioether formation: 2 Cell-Cl + HS-R-COOK + KOH $\longrightarrow$ Cell-S-R-COOCell + 2KCl + H_2O. It has been previously shown by Rogovin and Polyakov (8) that tosylcellulose reacts at elevated temperatures with sodium salts of carboxylic acids to form cellulose esters. In most instances, the known reactions of chlorocellulose and tosylcellulose are quite similar.

Marked decreases in chlorine and sulfur contents were obtained in most cases by the use of too high a reaction temperature (table 3). This was apparently due to removal of chlorine atoms by alkaline hydrolysis occurring as a side reaction.

Table 3. — Reaction of chlorocellulose yarns with thioacids

Sample	Mercaptoacid	Temp.	Breaking strength	Elongation	Breaking strength retention[1]	Tenacity	Energy to rupture	S[2]	Cl	Moisture	Ash	Cuene Soly.[3]	Methylene blue dyeing[4]
		°C.	Lb.	Pct.	Pct.	G./tex	Lb.	Pct.	Pct.	Pct.	Pct.		
1	$HS\text{-}CH_2\text{-}COOH$	60	5.0	28.1	90	9.9	4.4	1.4	2.7	12.2	2.3	BD	+++
2		80	5.6	31.3	100	9.8	5.7	3.2	1.6	12.2	3.9	BD	++
3		100	3.8	38.4	69	6.9	3.9	2.7	1.1	12.4	1.3	BD	+++
4	$HS\text{-}(CH_2)_2\text{-}COOH$	60	5.5	33.6	98	10.9	5.3	1.5	2.6	11.5	2.7	B	++++
5		80	4.6	28.0	82	8.6	4.3	2.9	1.8	11.5	4.1	BD	++++
6		100	4.3	37.8	77	7.9	4.1	2.5	1.3	11.7	1.9	B	++
7	$HS\text{-}(CH_2)_3\text{-}COOH$	60	5.5	32.4	98	10.7	5.0	1.6	3.7	10.9	2.4	SB	+++
8		80	4.1	31.5	55	5.6	2.6	2.7	1.7	11.1	3.3	B	++
9		100	3.0	32.7	72	7.8	3.6	2.3	1.2	11.3	2.1	B	++
10		60	6.1	27.6	109	12.0	5.3	3.1	2.2	10.8	3.1	BD	++++
11		80	6.0	30.3	107	10.7	5.5	2.3	1.6	12.8	3.7	B	++
12		100	5.5	31.8	98	10.0	4.9	2.5	1.1	11.6	1.9	SB	++
13	$CH_2\text{-}COOH$	60	4.7	40.7	85	7.9	4.9	1.3	2.8	11.9	3.7	B	++++
14	|	80	3.4	37.7	60	5.4	3.9	2.4	1.8	13.3	6.2	B	+++++
15	$HS\text{-}CH\text{-}COOH$	100	3.1	44.3	56	4.8	4.0	2.3	1.3	12.2	7.1	B	++++
16	None	-	4.3	24.9	78	9.6	3.0	0.6	4.6	10.6	0.1	D	+
17	None[5]	-	5.6	12.1	(100)	17.5	2.3	-	-	-	-	D	2

1/ Compared to sample 17.

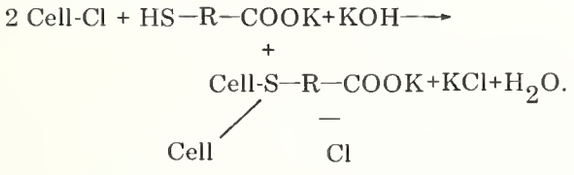
2/ Analyses are corrected for moisture and ash.

3/ D = dissolved.
B = ballooned.
S = swollen.

4/ Range: faint to deep blue.

5/ Untreated kiered yarn.

The affinity of the treated yarns for methylene blue confirmed in a qualitative way that carboxyl groups were present. However, the intensity of dyeing did not correlate as well with the sulfur content as might have been expected. Since cellulose cross-linking usually imparts a resistance to dye absorption, it is possible that the effects of the carboxyl groups were partially cancelled by crosslinking. A further complication is the possible formation of sulfonium salts:



This type of reaction also would decrease the affinity of the yarns for methylene blue.

Properties of thioether yarns. — With all of the aliphatic monocarboxylic mercaptoacids, a breaking strength retention of 90 to 100 percent, based on untreated kiered yarn, was obtainable at sulfur contents of about 1.5 percent. The strength retention based on chlorocellulose yarn was 117 to 130 percent. Such a high strength retention after two consecutive substitution reactions at the same cellulosic reaction sites is unusual. These and other properties are shown in table 3.

Reaction with an aromatic mercaptoacid, o-mercaptobenzoic acid, resulted in 98 to 109 percent retention of the breaking strength of kiered yarn even at sulfur contents of 2.5 to 3.1 percent. Based on chlorocellulose yarn, the strength retention was 127 to 141 percent. At high sulfur contents, only 2-mercaptoacetic acid in the aliphatic series of acids showed analogous effects.

With a dicarboxylic acid such as 2-mercaptosuccinic acid, strength losses of 15 to 44 percent, based on untreated kiered yarn, were observed. However, at the lowest sulfur content studied (1.3 percent), the breaking strength was still 9 percent greater than that of the chlorocellulose yarn used in the preparation.

The conversion of chlorocellulose yarn to carboxyalkyl- or carboxyaryl-thiocellulose resulted in considerable swelling over and above that occurring in the preparation of the chlorocellulose. This is evident from the high elongation-at-break (28 to 44 percent) of the treated yarns. The greatest elongation (38 to 44 percent) was obtained with the dicarboxylic acid, 2-mercaptosuccinic acid which suggests that the amount of swelling increased with the number of carboxylate groups introduced.

Although the tenacity values of the treated yarns were considerably lower than those for untreated kiered yarn, they equalled, in a number of instances, the tenacity of chlorocellulose yarn from which they were made. Monocarboxyalkylthiocellulose yarns having a sulfur content of 1.5 percent retained 103-114 percent of the tenacity of chlorocellulose yarn. 2-Mercaptoacetic acid and o-mercaptobenzoic acid treatments resulted in 102-125 percent retention of tenacity at sulfur contents as high as 2.5 to 3.2 percent.

The energy-to-rupture was generally much higher in the carboxyalkyl- and carboxyaryl-thiocellulose yarns than in either the chlorocellulose yarn or untreated yarn. The increased elongation of the products is largely responsible for this effect.

As shown in table 3, the moisture content of the carboxyalkyl- and carboxyaryl-thiocelluloses were slightly higher than for chlorocellulose. This is a further reflection of the additional swelling that occurred in their preparation, and the presence of ionic, hydrophilic substituents in the products. The observed high ash contents are due to the cation-exchange groups which were introduced in their potassium form.

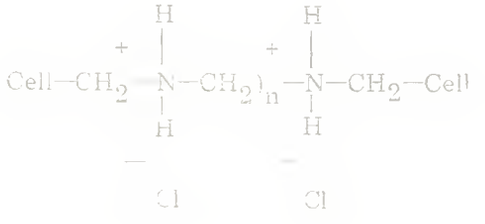
Reaction with primary diamines. — Chlorocellulose yarns were reacted with pure primary, secondary, and tertiary amines at 105° for 2 hours. As evidenced by receptivity to acid dyes such as Kiton Fast Red, only the primary amine (ethylenediamine) reacted. The secondary amine (N-ethylcyclohexylamine) and tertiary amines (triamyl amine and N, N, N', N'-tetramethylethylenediamine) failed to react under these conditions.

The inability of chlorocellulose to be quaternized by tertiary amines was also observed by

Battaglino and others (1). While cellulose chloroacetate underwent quaternization, the chlorocellulose (prepared by reaction of cellulose with thionyl chloride in chloroform) failed to react. However, Kryashev and others (6) were successful in quaternizing cellulose tosylate with pyridine. Some differences in reactivity of cellulose tosylate and chlorocellulose are to be expected, since tosylate is a better leaving group than chloride.

Three primary diamines were selected for reaction with chlorocellulose yarns: ethylenediamine, 1,4-butanediamine, and 1,6-hexanediamine. The order of reactivity of the three primary diamines with chlorocellulose yarns was: ethylenediamine (EDA) > 1,4-butanediamine (BDA) > 1,6-hexanediamine (HDA). This order was observed at amine concentrations of 10 and 50 percent. With 10 percent EDA, one-fifth of the chlorine atoms were replaced (see table 4); however, with 10 percent BDA and 10 percent HDA, very little displacement occurred. With 50 percent EDA, almost two-thirds of the chlorine atoms were displaced by the diamine (percent N = 2.2, percent Cl = 2.0), while about a third of the chlorine was displaced with 50 percent solutions of BDA and HDA.

The extent of reaction of the chlorocellulose yarns with the diamines was also reflected in the change in cuene solubility and receptivity to acid dyes. All yarns that had been reacted with 50 percent solutions of the amines were dyed a deep shade of red with Kiton Fast Red, while lighter shades were obtained with yarns treated with 10 percent amine solutions. The cuene solubility of yarns treated with 50 percent diamine was low, since in all cases only swelling occurred. With 10 percent diamine solutions, the resultant yarns ballooned, and in some instances, dissolved in cuene. The insolubility in cuene is consistent with cross-linked diaminodeoxycelluloses of the general formula



are formed, and that optimum cross-linking as well as reaction occurs when n = 2.

Properties of diaminodeoxycellulose yarns. — The breaking strength of yarns reacted with the diamines was 96 to 114 percent of the strength of the chlorocellulose yarn used for their preparation. Except at very low nitrogen contents, their strength was less than that of untreated kiered yarn. The strength retained was relatively independent of the chain length of the diamine used, for a given percentage of nitrogen introduced.

The use of 50 percent solutions of the diamines caused a slight yellowing of the yarns. However, it was necessary to use this concentration to obtain high nitrogen contents (1.0 to 2.2 percent).

The elongation-at-break of the treated yarns was high (31 to 37 percent), although appreciably lower than that of the chlorocellulose yarn used. The cellulose cross-linking that occurred was undoubtedly responsible for this decrease. The tenacity of the treated yarns was 102 to 122 percent of that for the chlorocellulose. The energy-to-rupture was only slightly affected by the amination treatment and remained more than double the value for untreated, kiered yarn.

The moisture content of diaminodeoxycelluloses at nitrogen contents of 1.6 to 2.2 percent was slightly higher than that of chlorocellulose. Samples containing only 0.7 to 1.0 percent nitrogen showed the same moisture content as chlorocellulose yarn.

Chemical properties of the diaminodeoxycellulose yarns are still under investigation. They are expected to have high reactivity, based on properties previously observed for aminoethylated cotton (9).

CONCLUSIONS

Chlorodeoxycellulose can be prepared in fibrous form by the reaction of thionyl chloride with activated yarn in dimethyl formamide. The chlorine content of the yarns is dependent on the thionyl chloride concentration and the

Table 4. — Reaction of chlorocellulose yarns with primary diamines

Sample	Amine	Amine concn.	Breaking strength	Elongation	Breaking strength retention[1]	Tenacity	Energy to rupture	N	Cl	S	Moisture	Ash	Cuene soly.[2]	Kiton red dyeing[3]
		Pct.[4]	Lb.	Pct.		G./tex	Lb.	Pct.	Pct.	Pct.	Pct.	Pct.		
1	NH_2-$(CH_2)_2$-NH_2	10	4.8	35.1	81	9.4	4.7	0.7	4.1	0.5	8.8	0.7	SB	+++
2		50	4.9	30.7	83	9.3	4.5	2.2	2.0	0.1	9.8	0.7	IS	++++
3	NH_2-$(CH_2)_4$-NH_2	10	5.3	36.3	90	10.1	6.0	0.2	5.0	0.6	9.9	0.3	B	+++
4		50	5.0	32.8	85	9.5	5.0	1.6	3.3	0.2	10.3	0.4	S	++++
5	NH_2-$(CH_2)_6$-CH_2	10	5.7	36.6	97	11.1	6.4	0.3	5.2	0.7	7.8	0.3	D	++
6		50	5.1	33.0	86	9.8	5.1	1.0	3.1	0.2	8.2	0.3	S	+++
7	None	-	5.0	43.2	85	9.1	5.6	-	5.0	0.6	8.6	0.5	D	+
8	None[5]	-	5.9	12.8	(100)	17.7	2.3	-	-	-	-	-	D	+

[1] Compared with sample 8.

[2] I = Insoluble. B = ballooned.
S = Swollen. D = dissolved.

[3] Range: faint to dark red.

[4] In n-butanol.

[5] Untreated, kiered yarn.

reaction time. The chlorocellulose yarns possess some rot resistance, with this resistance being directly proportional to the chlorine content.

The chlorocellulose yarns react with mercaptoacids to form cross-linked cellulose thioether-esters. Aromatic mercaptoacids such as o-mercaptobenzoic confer the most favorable tensile properties. For reaction with aliphatic mercaptoacids, the optimum reaction temperature is 60 to 80°. Above this temperature, alkaline hydrolysis causes removal of chlorine and decreased thioether formation.

Chlorocellulose yarns react with primary aliphatic diamines to give cross-linked diaminodeoxycelluloses which are insoluble in cuene and receptive to acid dyes. Maximum cross-linking occurs with ethylenediamine. Secondary and tertiary aliphatic amines fail to react with chlorocellulose, as has been previously reported by other investigators.

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DISCUSSION

QUESTION: Do the chlorocellulose yarns exhibit any flame resistance?

MR. T.L. VIGO: When burned from the top (at 0° angle), they were self-extinguishing and left a carbonaceous residue. However, they failed to pass the standard vertical flame test.

QUESTION: A way to impart flame resistance would be to react chlorocellulose with trimethyl phosphite by way of the Arbuzov rearrangement.

MR. T.L. VIGO: I believe this reaction has already been carried out by Russian investigators and substantial flame resistance has been obtained.

QUESTION: Did you try to modify cellulose with the bromine analog, that is, thionyl bromide? This should impart substantial flame resistance.

MR. T.L. VIGO: No, but it should give the properties you mentioned. However, thionyl bromide is quite expensive compared with thionyl chloride.

CHAIRMAN: The overall treatment at this exploratory stage is quite expensive, so the use of thionyl bromide would not be prohibitive.

QUESTION: Are the chlorocellulose yarns stable to normal hydrolysis?

MR. T.L. VIGO: Yes. As evidence for this stability, one of the wash steps involves immersion in dilute ammonium hydroxide solution. It is difficult to displace more than 70 percent of the chlorine even with good nucleophiles, as was shown in this talk.

THE CONTRIBUTION OF COTTON TO RURAL AREAS DEVELOPMENT

BY

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Baton Rouge, La.

If you had your choice, would you pay $75,000 to $100,000 for a small man-made lot near New Orleans, or would you purchase a much larger tract of land in an area with plenty of space, with room to grow and with access to the Gulf Coast area?

The answer is very simple. First, very few of us here today have $75,000 ready cash. And if we did have that much, we would think several times before spending it for a status symbol. Yet, realtors in this area have no problem finding buyers for this property.

Hopefully, within the next 10 years, people will be moving back to the rural areas and the slums of our larger cities will have been eliminated. We are fortunate to live at a time and be in a position to be a part of the greatest movement in the history of our country—the move back home, to the country. Opportunity has traditionally been associated with the big city. But, today, there appears to be another side of the story. The side about poverty in the Ghettos, rats taking over, and the need for the enlightened people of this country to bring their talents to town and help educate the poor people in the slums, and encourage them to put down the torch that burns and destroys, and take up the torch of knowledge.

But there is a better way. You don't kill a noxious weed by clipping the top of it off. You pull it up by the roots, don't you? Then it is logical to assume that poverty, Ghettos, slums, and riots can only be eliminated by cutting off the flow of people to the cities and beginning a movement back to the country. And that's where Rural Areas Development comes in.

The rural areas must be developed to provide all the advantages found in large cities, plus the

privilege of being closer to nature. Smaller communities are springing up all over the Nation. They provide education, hospitals, electricity, good roads, streets, churches, transportation, entertainment, culture, recreation, employment, and just about everything it takes to satisfy the wants of modern man. I say all this to remind us of the importance of developing our rural areas. Rural development has had top priority in the USDA and LSU for over 12 years. It is very important to many people.

This brings us to "The Contribution of Cotton to Rural Areas Development." How could cotton contribute to Rural Areas Development? Cotton invented the idea in a certain sense. Because, had cotton not been an important crop, the rural areas in this State would have been slow in developing. And if the cotton economy had held strong, we wouldn't be worrying about RAD today.

The value of cotton to Louisiana reached 130 million dollars in 1968. This includes the value of seed, lint, government payments, and processing.

Over 400-thousand acres of cotton were harvested in Louisiana last year. An average of 664 pounds of lint per acre was achieved from the nearly 545-thousand bales produced last year.

In terms of dollars and cents, the 1968 cotton crop was worth more than $83-million in lint and seed. Jobs for our rural people were provided at 190 gins, 25 warehouses, or compresses, or both, 8 oil mills, 8 seed distribution outlets, and 8 other warehouse facilities.

If we were to take a typical parish with a 32 thousand-acre allotment, we would find that last year cotton farmers in that parish bought approximately 826 thousand dollars worth of chemicals and insecticides and spent 765 thousand dollars for fuel, repairs, and equipment supplies. In addition, these farmers purchased 703 thousand dollars worth of equipment for production purposes.

Labor utilized was 11.52 hours per acre. This amounted to 368,640 hours for the 32,000 acre allotment. At 9 hours per day, 40,960 man days were utilized. At $1.30 per hour, 475 thousand dollars were spent for labor. They paid local ginners a bill of $736,000 just to gin their cotton. If they had borrowed 75 percent of their operating capital, they would have paid to local lending institutions an annual rental rate for funds of about 240 thousand dollars.

In addition, these cotton farmers had a return to land and management of 3.5 million dollars to invest or spend. In total, therefore, this one 32 thousand-acre allotment meant an injection of some $9,750,000 into the mainstream of the local economy. It is not difficult to multiply this figure by the number of parishes which depend largely upon cotton for their economic prosperity.

You and I know that the dollars spent in a given trade area change hands several times. For example, the farmer pays the service man for repairs to his tractor, the service man pays the grocer for his food, the grocer pays the wholesaler, and so on—multiplying itself many times. So, if only 50 percent of the total were to remain in the parish and change hands three times, the 32 thousand-acre cotton allotment could mean nearly 15 million dollars to the local economy. If we were to break this down into the form of basic needs, it could mean over 3,925 jobs, paying $5,000 a year each.

Also of great economic importance are the business firms directly related to cotton—gins, oil mills, de-linting plants, cotton compresses, and warehouse facilities. These represent an investment of over 80 million dollars and employ thousands of people.

In addition, there are approximately 30 cotton merchants and firms located in Louisiana and these employ hundreds of people, representing sizeable investments in facilities.

Going beyond those businesses directly related to cotton, we would find even more firms dependent on the production of cotton for their existence. Actually, the farm value of cotton represents only about 15 percent of all the consumer's dollar that is spent for cotton products. The other 85 percent represents business created in processing, handling, financing, and distributing these products. This represents hundreds of firms, providing employment to thousands of persons.

On this basis, the 130 million dollar Louisiana cotton crop represents a consumer expenditure for cotton products of approximately 736 million dollars. Much of this business is generated outside Louisiana, but still many Louisiana firms share in it. These activities further bolster the total economy of the State.

The cotton farmer's contribution to rural progress is seen in the development of better highways and farm roads, electricity, and telephones throughout the countryside, and modern medical facilities in most communities of any size. The progressive cotton farmer is a joiner. He is active in civic affairs, as well as such organizations as the Farm Bureau and the National Cotton Council, to mention a few.

Your Louisiana Cooperative Extension Service is a partner in progress with the farmer and the rest of the cotton industry. Through the county and home demonstration agents, Extension is striving to increase production in the fields while seeking new and expanded uses for the product in the marketplace.

Cotton plays an integral role in Extension's Giant Step program of rural areas development. In its 5-year projection, we envision the yield per acre to grow from the 1963 to 1966 average of 579 pounds to 750 pounds by 1972.

This upward climb has been evident in recent years. The average in 1966 was 602 pounds of lint per acre, in 1967 it was 621, and last year it was 664. At this rate, we do not believe our projection of 750 pounds by 1972 to be overly optimistic.

We recognize that the cotton industry has had its problems in recent years. And we know that increased production is not the sole answer to these difficulties.

The use of cotton on both the domestic and foreign markets has dropped significantly in the last couple of years. The basic reason for this downward slide has been an increased use of man-made fibers. In 1968, for example, cotton's share of the total fiber market was slightly less than 44 percent. This compares with 49 percent in 1967 and higher percentages in preceding years.

It appears to us that there are three primary ways of stemming this tide and increasing the amount of cotton used each year. First, cotton must regain its share of the fiber market that has been lost to man-made fibers. The advertising effort made possible through the recently enacted Cotton Research and Promotion Act is one step in the right direction. But even this will be an uphill fight because of the enormous advertising budgets of the large corporations backing synthetic fibers.

Secondly, the United States government can aid in the disappearance of U.S. cotton by increasing imports. This will not be easy, however, because many foreign countries have increased their cotton production in recent years. Of course, increased foreign production means increased competition for the U.S. cotton industry.

Unless a program is created, whereby U.S. cotton can be offered to foreign interests at lower costs than is now the case, it appears unlikely that our exports will increase to any appreciable degree in the next few years.

The third way by which more U.S. cotton can be used is through the development of improved processes for utilizing present cotton commodities and by the development of totally new uses for cotton fiber.

This search for new uses is a challenge to you gentlemen dedicated to the research aspects of the industry. I noticed in a recent issue of the Delta Farm Press, an editorial exploring the use of nonwoven cotton in the expanding market of disposables, such as sheets and pillowcases for institutional use.

Gaylon Booker, who is assistant market research director for the NCC (National Cotton Council), suggests that a 1 percent penetration of the institutional bed linen market by disposables would amount to 100-thousand bales. He says this would double fiber requirements for institutional sheets and pillowcases.

Other potentials in this area include disposable towels, wash cloths, medical gowns, surgical pack materials, diapers, aprons, smocks, wiping cloths, and table linens.

Since cotton's present quality disadvantages in the disposable field are directly related to cost and processing economics, Mr. Booker recommends that initial research be aimed at cost reduction. His research suggestions include: (1) Developing more economical processes for cleaning and bleaching staple cotton, (2) improving fiber length uniformity, and (3) developing fabric-forming processes that would be more adaptable to the cotton fiber.

These proposals and other research ideas which will improve cotton's posture on the market directly confront each of you. And not only must you come up with new uses for cotton, but these uses must be produced on a competitive level with other types of fibers in order for cotton to maintain or improve its position in the American economy.

Finally, while we often tend to get preoccupied with the big picture, let's not overlook the grass-roots beneficiary of all our efforts, the rural resident whose basic economy is centered on the welfare of the cotton industry.

Many rural counties and towns prosper or lose in proportion to the successes or failures of the cotton crop and its markets. We're talking about the many banks, dry goods stores, drug stores, gins, equipment dealers, agricultural suppliers, automobile dealers, corner cafes, and even churches, which depend largely on this one agricultural commodity.

Therefore, any contribution that you or any other agriculturist makes to increase the uses of cotton will be reflected all the way down to Main Street, U.S.A. This, then, is the challenge I leave with you ... to seek new and revolutionary ways of adapting nature's most wondrous fiber, cotton, so that rural America will continue to prosper.

FOURTH SESSION: Elias Klein, Gulf South Research Institute, New Orleans, La., Chairman

THE DIMENSIONAL PROPERTIES OF KNITTED WOOL FABRICS: PART III. THE PLAIN-KNIT STRUCTURE IN MACHINE WASHING AND TUMBLE DRYING

[SUMMARY]

by

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(Presented by W. Fong)

The first papers of this series proposed a definition and means of attaining the fully relaxed state of plain-knit wool fabric. This paper establishes the validity of this definition, which is shown to differentiate, precisely, relaxation shrinkage owing only to loop shape changes from felting shrinkage or fiber migration to a more compact state without loop distortion. This discrimination is achieved by analyzing dimensions of the same fabrics tested in Part I (Textile Res. Jour. 38: 999(1968)) through a series of 10 wash and tumble-dry cycles.

We observed that dimensional changes from the dry relax state to the fully-relaxed state depend upon loop length and yarn count, and to a smaller extent, on fiber fineness and yarn twist, but not at all on the shrink-resist treatment level. These changes always resulted in a decrease in length and width during relaxation.

Analysis of subsequent dimensional changes from the fully relaxed state through multiple washing and tumble drying cycles shows that: (1) for treated yarns spun from Wurlan shrink-resist treated top, area shrinkage increases linearly with the number of wash and tumble dry cycles, but nonlinearly for untreated yarns; (2) for untreated yarn, shrinkages in length, width, and area depend on fiber quality, yarn twist, loop length, and complex interactions among these variables; (3) at a low treatment level, linear and area shrinkage depend to a less extent on all of these variables; (4) at high treatment level, the Wurlan treatment of wool top adequately restricts felting to within an acceptable 8-percent area shrinkage limit; in this case, changes in dimensions from the fully relaxed state are independent of all fiber, yarn, and fabric variables.

In summary — our wash data, obtained by a relatively severe test procedure (10 cycles of washing and tumble drying in regular automatic home laundering equipment), demonstrate conclusively that completely satisfactory stability can be achieved in a plain-knit fabric independent of wool quality and yarn and fabric constructional parameters by resin treatment of wool top based upon the Wurlan interfacial polymerization procedure. However, regardless of level of shrink-resist treatment, yarns spun from treated top still exhibit a high degree of relaxation shrinkage similar to untreated wool. Consequently, any machine-washable and tumble-dryable knit made from treated top must still be wet-relaxed and tumble-dried to insure completely stable garment dimensions.

CHEMICALLY STABILIZED AND WRINKLE-RESISTANT COTTON CIRCULAR KNITS

by

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(Presented by B.A.K. Andrews)

ABSTRACT

Finishing agents are known to impart stabilization to cotton knit fabrics. In this investigation crosslinking agents and hand modifiers are used to produce dimensionally stable cotton knit fabrics with durable-press properties.

Variation of the crosslinking agent to stiffening agent ratio will produce fabrics with a wide range of dimensional stability, stiffness, and smooth-drying properties. These results are compared with those obtained on treatment of selected woven fabrics. The optimum concentrations are proposed, and the use of the finish in post curing is discussed. Laundering studies of the finish on different constructions show the durability of the durable-press all-cotton knits to exceed that of the all-cotton wovens investigated.

INTRODUCTION

The end use available to knit fabrics are increasing at a dramatic pace. In addition to women's dress and sport clothes, men's dress shirts, slacks and suits are now accepted markets for knits; previously only woven goods occupied these markets.

There are economic advantages in making fabric by knitting rather than weaving. Knitting machines operate much faster than looms, and the slashing and desizing steps are omitted in fabric preparation.

Major disadvantages of cotton knits in many clothing end uses are their limpness, lack of dimensional stability and inability to hold a sharp crease. The present work explores the possibility of chemical finishing to increase dimensional stability, smooth drying properties and wrinkle resistance, and to change the hand and drape of the circular knit fabrics without affecting comfort and resistance to abrasion damage inherent in the knit structure. Mechanical stabilization, such as compaction will not be considered in this study.

Experimental and results. — Three circular knit cotton fabrics were used in this study: a 5.2 oz/yd.^{2} cable stitch construction, a 5.3 oz./yd.^{2} and a 4.1 oz./yd.^{2} honeycomb construction. Two woven fabrics, a 7 oz./yd.^{2} twill and a 4.8 oz./yd.^{2} oxford were included for comparison. Dimethylol ethyleneures, catalyzed by $MgCl_2.6H_2O$ used as 30 percent on weight of crosslinking agent, and dimethylol dihydroxyethyleneurea, catalyzed by $Zn(NO_3).6H_2O$ used as 10 percent on weight of crosslinking agent were used to study the processing variables. One-half percent emulsified polyethylene was included in the treatments as a fabric softener, and three percent low molecular weight, low acetyl content polyvinyl alcohol was included as a hand builder.

The agents were applied to the fabric in the usual manner of padding, drying, and curing at elevated temperatures. The woven fabrics were dried and cured at original dimensions. The knit fabrics were dried and cured with about 5 percent stretch in each direction. This stretch produced a tension which gives the best wash-wear rating and dimensional stability under laboratory conditions.

Standard test methods, analyses and laundry procedures were used to elevate the finished cotton fabrics.

Maximum wash-wear ratings, by the AATCC overhead lighting method, can be obtained with the lowest concentration of dimethylol ethyleneurea used — 3 percent. Application

from a 10 percent treating solution does not significantly increase the ratings (from 3.6 to 3.7). In fact, an acceptable wash-wear rating can be obtained at a much lower level of treatment than is needed for dimensional stability. In the consideration of the wash-wear ratings, comparisons of the knits are made with standards designed for evaluation of woven fabrics. Because of the structure of the knits, it is more difficult to obtain the smoothness of the treated woven fabrics under the conditions of the test.

With crosslinking agent alone, the treated fabric is rather limp as judged from subjective observation and wales stiffness values (2.2-3.0 x 10^{-4} in. lb.) by using the Tinius Olsen Method. Addition of polyethylene reduces this low level of stiffness even further to 1.7 to 2.0 x 10^{-4} in. lb. Addition of 3-percent low molecular weight polyvinyl alcohol to the treating both produces knit fabrics with increased stiffness and a firmer hand. The degree of improvement is a function of both the polyvinyl alcohol and amount of crosslinking agent present. The wales stiffness values ranged from 2.2 x 10^{-4} in. lb. for a 3 percent crosslinking agent bath, to 6.5 x 10^{-4} in. lb. for a 5 percent bath and 10.0 x 10^{-4} in. lb. for a 10 percent bath. A sample of untreated cotton broadcloth tested for comparison had a warp stiffness value of 7.6 x 10^{-4} in. lb. The addition of polyvinyl alcohol to the finishing solution produces greater dimensional stability at lower levels of crosslinking than does the crosslinking agent alone. A cable stitch knit sample treated with 10 percent dimethylolethyleneurea has a shrinkage of 4 percent in the wales, the high shrinkage direction after a single laundering. Only 5 percent dimethylol ethyleneurea is needed to reduce the wales shrinkage to 3 percent if 3 percent polyvinyl alcohol is included in the pad bath. Untreated cable stitch knit fabric has a wales shrinkage of 17 percent.

Wash-wear ratings of the knit fabrics are changed little on laundering. After six home launderings, samples of cable stitch knit fabric treated with 5 percent dimethylolethyleneurea, polyethylene, and low molecular weight polyvinyl alcohol had a wash-wear rating of 3.3; those treated with 6 percent dimethylol dihydroxyethyleneurea, polyethylene, and polyvinyl alcohol had a wash-wear rating of 3.2. Ratings of samples line-dried after the spin cycle of the wash are slightly lower than those of tumble-dried samples. As would be expected, the nitrogenous crosslink is durable through these launderings; almost 100 percent bound nitrogen is retained.

To approximate in-use performance of the treated knit fabrics, trouser cuffs were fabricated from sensitized knit and woven fabrics and then cured. The cuffs were laundered 30 times and evaluated for resistance to damage by abrasion. The three knit constructions, treated with both crosslinking agent — polyethylene systems, with and without polyvinyl alcohol perform extremely well through the launderings. No abrasion damage is noted, even with the added stiffness imparted by the polyvinyl alcohol finish. The polyvinyl alcohol treatment improves the sharpness of crease rating of the cable stitch knit cuff from good to very good (on a poor, fair, good, very good scale) and of the honeycomb knit cuffs from fair to very good. Wash-wear ratings after 30 launderings were also improved by the polyvinyl alcohol treatment. Ratings of the cable stitch knit were improved from 3.7 to 4.0 and of the two honeycomb constructions from 3.8 to 4.1.

The wales stiffness values of the treated knit cuffs after 30 washes were inconsistent with subjective evaluation of the hand of the fabrics. Although the hand was firmer, the wales stiffness values for the cuffs of the three knit constructions treated with 5 percent dimethylol ethyleneurea-polyethylene-polyvinyl alcohol were lower than those treated with 5 percent dimethylol ethyleneurea-polyethylene alone (0.2 to 1.3 x 10^{-4} in. lb. lower). At these low stiffness values the sensitivity of the Tinius Olsen test may not be great enough to consider absolute values, but order of magnitude only.

The crosslinking agent-polyvinyl alcohol treatments cause strength losses (approximately 54 percent original bursting strength) as do conventional crosslinking treatments on woven fabrics. The polyvinyl alcohol obviates any strength improvements effected by the softener, but does not reduce the bursting strength more than does the crosslinking alone. Although these strength losses are more than the warp breaking strength losses shown by the treated twill fabric (15 percent) and treated oxford fabric (48 percent), the post cured knit cuffs retain a

superior abrasion resistance through 30 launderings. The twill cuffs treated with only 10 percent dimethylol ethyleneurea plus softener had seven major and three minor holes with first major damage after nine launderings. The oxford cloth cuff, an example of a light fabric, usually resistant to laundering shows minor abrasion damage after 27 launderings with two holes. But, the knit cuffs treated with 5 percent dimethylol ethyleneurea or 6 percent dimethylol dihydroxyethyleneurea, the low molecular weight polyvinyl alcohol and softener showed superior performance through the 30 launderings with little evidence of even minor damage. These cuffs had wash-wear ratings comparable with those obtained on the woven cuffs.

SUMMARY

Cotton knit fabrics can be treated, chemically, to improve dimensional stability and smooth-drying properties, and to change the hand and drape. Low levels of crosslinking treatments improve the wash-wear ratings, but higher levels are needed to achieve dimensional stability. Inclusion of polyvinyl alcohol produces increased dimensional stability at lower levels of treatment.

The polyvinyl alcohol additive also improves the sharpness of crease and crease retention of post cured, durable-press knit cuffs. Durable-press cotton knit fabrics so produced have an inherent abrasion resistance through at least 30 launderings. This asset, combined with the advantages contributed by the hand modifier serve to produce a superior end product that will compete with wovens in new end uses.

ACKNOWLEDGMENT

The authors wish to thank members of the Textile Testing Group and in particular,Mrs. Constance F. Cashen, Mrs. Sandra R. Danly, and Miss Kate Smith for the textile tests; Matthew J. Donoghue and Miss Gloria A. Gautreaux for the sample evaluation; and Mrs. Ann Black for the nitrogen analyses.

CROSSLINKING PRETREATMENTS OF GREIGE FABRIC FOR IMPROVED SMOOTH DRYING PROPERTIES OF DP COTTON

by

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(Presented by T.A. Calamari, Jr.)

ABSTRACT

An undesirable consequence of the rope bleaching of greige goods is the formation of longitudinal wrinkles which impair the appearance of the finished fabric even after resin treatment. By low level crosslinking of greige or desized goods before rope bleaching, it is possible to greatly reduce wrinkle formation and improve smooth drying performance of resin treated cotton fabric. The most effective treatments evaluated include a conventional pad-dry-cure treatment of desized fabric with DMEU, and a wet-dichloropropanol treatment of greige fabric. Optical bleaches must be used with both of these treatments to obtain satisfactory whiteness levels.

INTRODUCTION

Mainly for reasons of economy, speed, and convenience the rope method of bleaching greige goods has for many years been more widely employed by textile finishers than the open

width method. Because the wet fabric is squeezed while still in the rope form, longitudinal wrinkles are produced which remain tenaciously in the fabric throughout the various finishing operations. Even a final crosslinking treatment does not completely remove these creases. Although a durable-press sheet that has been rope-bleached does seem to be relatively wrinkle free, rewetting and redrying permits the internal stresses to relax and the rope marks to return. One approach to the problem is to use crosslinking agents to impart crease resistance to greige or desized goods before rope bleaching operations. It is this approach which is considered in the present study.

Experimental and Results

Fabric description. — The cotton fabrics used in this study were a greige and a desized 3.1 oz./yd.^{2} 80 x 80 printcloth, and a greige and a desized 4.0 oz./yd.^{2} 86 x 94 sheeting.

Chemicals. — The crosslinking reagents employed were dimethylolethylene urea (DMEU), dimethylol methoxyethyl carbamate (DMMEC), formalin, and 1,3 dichloro-2-propanol (DCP). Catalysts used were reagent grade magnesium chloride hexahydrate, zinc nitrate hexahydrate, and 35 percent hydrochloric acid. An alkylaryl-polyether alcohol was used as a wetting agent.

Processing procedures. — Crosslinking formulations containing DMEU or DMMEC were applied to greige or desized fabric using a conventional pad, dry, and cure technique. "Mild Cure" treatments with DMMEC were performed in the prescribed manner (3) except that a low solids level was employed. Wet (Form W) (2) and controlled moisture (Form D) (1) formaldehyde crosslinking treatments were performed using standard procedures. In both the "Form W" and "Form D" treatments, reaction time was varied to control the degree of crosslinking. Crosslinking with dichloropropanol was accomplished by padding the greige fabric through a solution of sodium hydroxide, then through an aqueous solution of DCP. The wet fabric was allowed to stand at room temperature overnight, after which it was neutralized with acetic acid then washed and dried. The crosslinked fabrics were then bleached by the rope technique either in the laboratory or in a commercial finishing plant.

Test methods. — For the most part, standard test methods, analyses, and laundry procedures were employed to evaluate the cross-linked bleached fabric. The standard smooth drying evaluation procedure had to be modified in that the test sample had to be evaluated with its warp direction both parallel and perpendicular to the overhead light which illuminated it. Rope marks are clearly visible only when they are viewed while being illuminated at a right angle. Since the rope marks are not very distinct when the sample is being viewed, while being illuminated by light parallel to the warp direction, the difference in the smooth drying rating obtained for each position is a measure of the severity of the rope marks.

Discussion. — Various crosslinking agents have been examined under a variety of treating and curing conditions. As expected, as the degree of crosslinking was increased, the resistance to wrinkle formation was enhanced. Losses in tensile properties and abrasion resistance became more serious. Strength losses were particularly large with the "Mild Cure," "Form W," and "Form D" treatments. An undesirable increase in fabric stiffness was observed with the pad-dry-cure treatment, the "Mild Cure" treatment, and one version of the wet dichloropropanol treatment (presumably owing to crosslinking of the starch sizing). Of the treatments examined, the dichloropropanol pretreatment resulted in a crosslinked greige fabric which had smooth drying properties equal to and tensile and abrasion properties better than those of any of the other pretreatments evaluated. Furthermore, when the caustic solution was applied before the DCP, the fabric hand was much better than that obtained in most of the other cases. Pilot-plant DCP treatments of this type were made with two lengths of greige sheeting using 3.75 and 7.5 percent DCP. They were then rope bleached by a commercial finisher. As expected, upon being given one standard wash and dry cycle both pretreated fabrics had significantly higher

smooth drying ratings than a nonpretreated rope bleached control. Longitudinal wrinkling was also much less pronounced than in the case of the control. After conventional crosslinking with DMMEC, the pretreated fabric retained a definite smooth drying superiority over a nonpretreated control crosslinked to the same N add-on. The pretreated samples were not as white as the nonpretreated controls either before or after the final resin treatment.

If any fabric stabilizing pretreatment is to be applied to greige fabric before rope bleaching operations, many finishers would prefer some type of conventional crosslinking treatment. A pad-dry-cure technique with DMEU can be employed if steps are taken to eliminate or reduce the excessively stiff hand that results from cross-linking the starch sizing. One method which can be used is to desize the greige fabric before low level cross-linking. Experiments on desized sheeting and print cloth have demonstrated that the problem of crosslink-induced stiffness was not encountered with these fabrics. Another method that gives satisfactory results and that eliminates the necessity for desizing before cross-linking is that of the high pressure steaming of the stiffened bleached fabric. Some resin is lost during steaming, but since the rope bleaching operation has been completed, this loss should not be serious. If this fabric is to be made into a durable-press finished product, a conventional crosslinking treatment at normal levels of resin add-on can be applied after steaming.

As pointed out above, it was not possible to commercially peroxide bleach the cross-linked greige fabric to the same degree of whiteness as that obtained with uncross-linked fabric. Laboratory and pilot-plant bleaching studies on greige and desized fabric give essentially the same result. Efforts to overcome this problem by overbleaching have not been successful; however, an acceptable product can be obtained by the incorporation of a small amount of optical brightener into either the cross-linking pretreatment or the final cross-linking treatment.

SUMMARY

The formation of longitudinal wrinkles during rope bleaching can be greatly reduced by cross-linking the greige or desized goods before the bleaching operations. Cross-linking provides the added fabric stability necessary to resist wrinkle formation. Conventional pad-dry-cure techniques can be used with DMEU and similar agents provided the cross-linking is carried out after the fabric is desized. If conventional treatments are applied to greige fabric, much of the agent is used up in cross-linking the starch resulting in a fabric with a very stiff hand. This stiffness can be removed by pressure steaming, but much of the cross-linking agent is also lost.

A much more satisfactory method of stabilizing greige goods is the application of a wet DCP cross-linking treatment. This technique consists in the padding of the greige fabric through a caustic solution several times, then padding it through an aqueous solution of DCP. The cross-linking of either greige or desized fabric makes it quite difficult to obtain satisfactory whiteness levels upon bleaching. The addition of 0.3 percent of an optical brightener to either the initial or to the final cross-linking formulation results in a fabric with an acceptable level of whiteness.

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cotton fabrics. In Proceedings of the Eighth Cotton Utilization Research Conference U.S. Dept. Agr., Agr. Res. Serv. ARS 72-70, pp. 87-93.

DISCUSSION

QUESTION: The durable press ratings you reported were average ratings of the samples viewed in two positions; that is, one with the longitudinal creases perpendicular to the floor, and the other with the creases parallel to the floor. What was the improvement in samples viewed in the latter case?

DR. CALAMARI: The rating was improved from 0.6 to 1.0 D.P. unit in this direction, whereas the average improvement over the two directions was 0.5 or 0.6 a D.P. unit.

QUESTION: Don't you feel an actual photograph of the samples would have demonstrated the improvements more clearly to the audience?

DR. CALAMARI: Perhaps it would have.

QUESTION: Can you vat dye on top of pretreated samples?

DR. CALAMARI: We have not tried dyeing any pretreated samples as yet, but we do not anticipate any trouble dyeing samples which have been cross-linked under wet conditions. Those samples which have been conventionally cross-linked would probably be difficult to dye evenly.

QUESTION: What resins do you recommend for the final durable press treatment?

DR. CALAMARI: For colored goods, a dimethyloldihydroxyethyleneurea-type cross-linking resin would be satisfactory. For white goods, a material like dimethylolmethyl carbamate would be more satisfactory.

QUESTION: Would the replacement of starch with polyvinyl alcohol simplify the pretreatment problem of induced fabric stiffness?

DR. CALAMARI: It might simplify the problem, but we have not tried it so we cannot say for sure.

QUESTION: Did crosslinking pretreatments cause any trouble in removing the natural coloration during bleaching?

DR. CALAMARI: Yes it did. After pretreatments with either conventional or wet cross-linking agents, the cross-linked samples were more resistant to bleaching than nonpretreated samples. However, the problem can easily be solved by the incorporation of 0.3 percent of an optical bleach into the final cross-linking pad bath.

A VAPOR-PHASE REACTION SYSTEM APPLICABLE TO EXISTING GARMENT CURING OVENS

by

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(Presented by Esmond J. Keating)

INTRODUCTION

The history of vapor-phase reactions involving cotton and various chemicals was presented at the Conference on the Vapor-Phase Finishing of Cotton held at the Southern Utilization Research and Development Division a little over two years ago. The proceedings of that Conference are a good bibliography on the subject up to that time. Since then, in the two plus years, a number of additional publications and presentations are on record. All of these publications point out the advantages of vapor-phase processing.

This paper deals particularly with vapor-phase cross-linking of cotton with formaldehyde, but it is conceivable that the techniques to be reported could be used for other reactions as well.

Figure 1 shows the apparatus used first in an attempt to get a direct comparison of the results produced by using various formaldehyde donors and catalyst. It consists of a three-liter glass resin kettle with a matching electric heating mantle. The cover with its standard four openings, made insertion of a thermometer, various reagent inlet tubes, and vent very convenient. No forced agitation was provided in order not to complicate an already complex system. As it turned out, the natural circulation was adequate for surprisingly uniform reactions. All samples were checked for uniformity by dyeing with a direct cotton dye. The fabric samples were mounted on a stainless steel screen wire cylinder as shown in the lower right of the picture.

The usual operating procedure was to heat the vessel to the desired temperature, introduce or start the reagent flow of both donor and catalyst, and, after a short interval, remove the lid to insert the fabric samples. The reagent and catalyst flow was continued throughout the reaction time.

The reagents investigated using this apparatus are shown in table 1.

The formaldehyde donors include paraformaldehyde, methyl formcel, trioxane, and formalin. The materials listed under the heading "Promoters" were used to promote the decomposition of the donors.

Listed with the vapor-phase catalysts is sulfite salts. These salts are not vaporizable but were used as sulfur dioxide donors. Detailed results obtained with all of these materials will be published at a later date since they are not the subject of this paper.

During the investigations with these reagents in the glass apparatus shown, there was a constant awareness of some problems with the procedures that made a knowledgeable analysis of the entire system difficult, if not impossible. Some of these problems were: difficult temperature control during startup and operation; temperature differentials within the reactor, such as the lid being a different temperature than the walls despite efforts to heat or insulate it. This caused condensation and repolymerization of vapors defying accurate knowledge of concentrations in the vapor. Another and most serious flaw was the disturbance caused by introducing and withdrawing samples. Even a special lid with slots for introducing the samples would not have completely eliminated the disturbance and the possibility of losing vapors and introducing some air into the system. For this reason, the concentration of vapors could not be estimated with any degree of confidence.

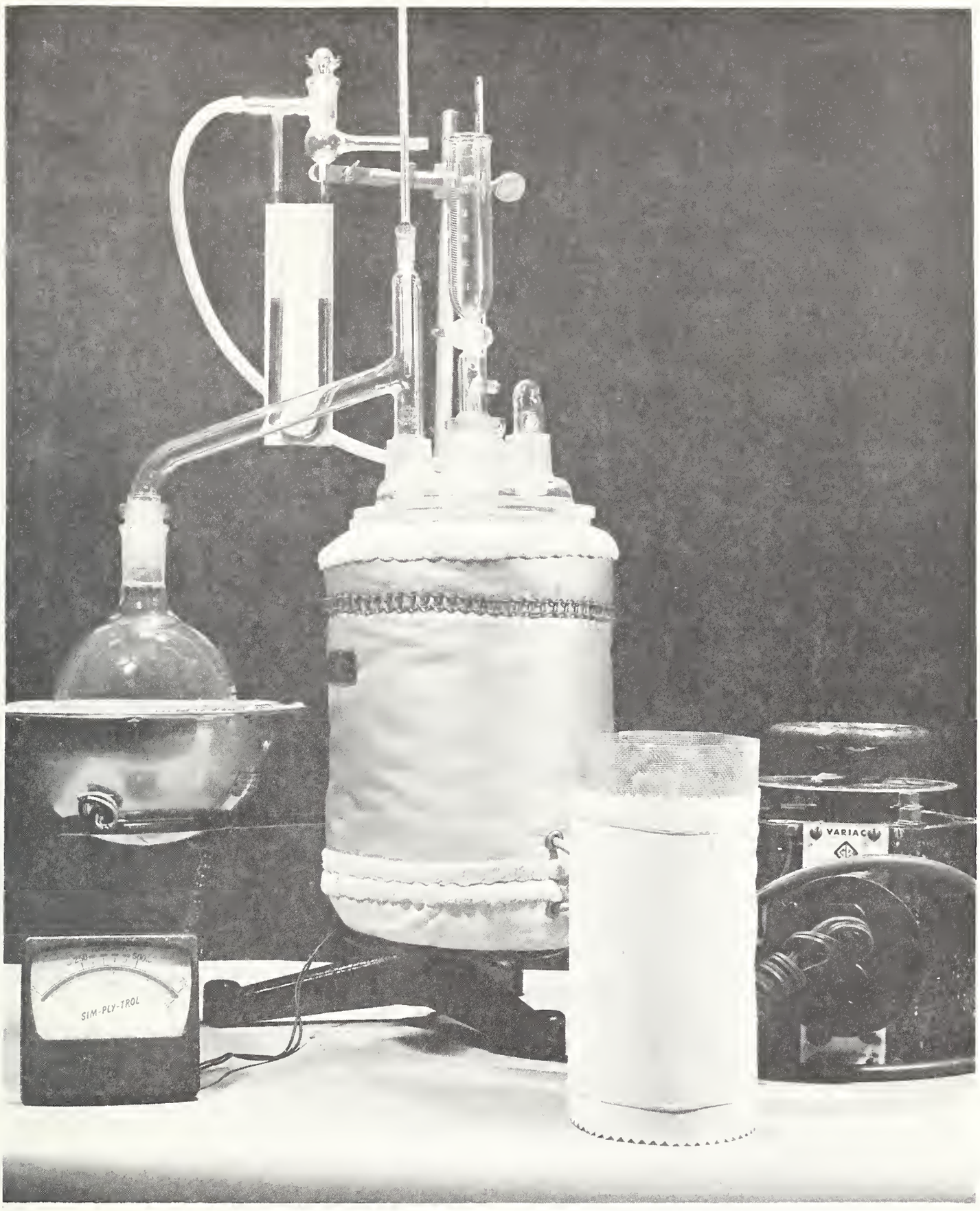

Figure 1. — Three-liter glass resin kettle with matching electric heating mantle.

Table 1. — Reagents investigated

Formaldehyde donors	Promotors	Catalyst	
		Vapor phase	Preimpregnated
Paraformaldehyde Trioxane Methyl formcel Formalin	Sulfuric acid Phosphoric acid Acetic acid Oxalic acid Borax Sodium hydroxide	Formic acid Sulfur dioxide Hydrogen chloride Sulfite sales (SO_2) Methyl bromide Chloramine T	Magnesium chloride — citric acid Triphenylmethyl hexaflorophosphate Triphenylmethyl hexafloroarsenate Triphenylmethyl hexafloroantimoniate

Despite these problems, some data were obtained on the relative merits of the reagents. For instance, of the catalysts used, HCL was by far the most active for the desired cross-linking, but also the most active for the undesired attack on metals in and around the apparatus. Another conclusion was that sulfur dioxide was the next best vapor catalyst--being adequate with respect to rate and amount of reaction, wrinkle recovery, subjective tests such as smooth drying and tear resistance, and was far less corrosive to the equipment.

A third conclusion, based, of course, on this particular system, was that paraformaldehyde was a troublesome donor because of the relative stability of the solid and the repolymerization characteristics of the vapor.

Some of the results that contributed to these and other conclusions are shown in figure 2.

These are composite reaction rate curves at three temperatures, using three formaldehyde donors, with SO_2 as catalyst at three levels of feed rate and on the other plane the wrinkle recoveries imparted to the fabric samples under these conditions. The values for the three levels of SO_2 catalyst are combined into the single curve shown for each donor at each temperature. The letter on each curve indicates the donor used. These curves point out the need to consider the overall system before interpreting results. For instance, the rate curves indicate that vapor from paraformaldehyde is not nearly as reactive as the vapor from the other donors. This is not necessarily true and is probably due to differences in concentration which were not readily measurable. The wrinkle recoveries could also reflect similar inequities and caution must be exercised in making comparisons.

It was evident that a different system had to be devised in order to eliminate these uncertainties. A closed system was considered and introduction of the SO_2 catalyst, uniform heating and the pressure increase were major factors of contention. The catalyst additon was simplified by the fact that SO_2 was readily soluble in aqueous formaldehyde solutions.

Heating in a hot-air oven seemed to be the simplest approach to achieve uniform temperatures, but alleviation of the pressure buildup was not obvious. Rapid heat transfer was desirable so a thin-walled container was considered but the expanding gases and vapors would have to be reconciled. Since a thin wall would not ordinarily withstand the pressure buildup anticipated, one answer was an expandable container, not necessarily stretchable, but having pleats or excess material that would allow for expansion to a larger volume. The common plastic bag could not be readily overlooked. The technique we settled on is shown in figure 3.

The original apparatus made use of a hardware cloth frame shown upright in the center to hold the samples. It allowed some circulation before the system reached its final volume. The samples were suspended within the frame. Originally, the chemicals were placed in the bottom of the bag and then in a separate smaller perforated bag, fastened to the top of the frame. These techniques failed to give uniformity. It was felt that if the reagents were spread over an

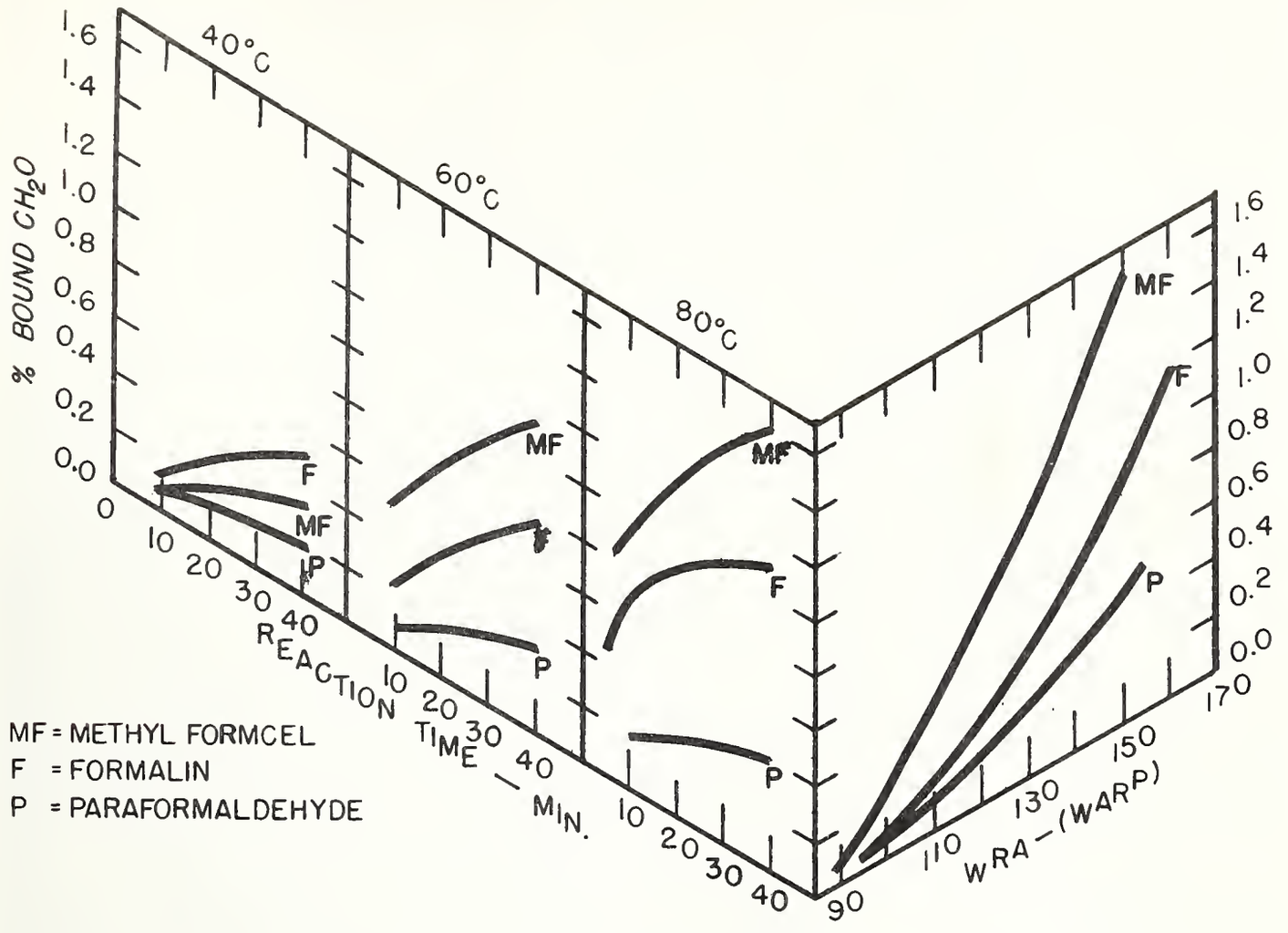

Figure 2. — Composite reaction curves.

extended area it would increase the rate of vaporization and give uniform reaction. Glass fabric offered a convenient means of achieving an extended surface. It proved to be excellent. The liquid reagent was spread on the glass cloth by spraying and weighed accurately to 0.1 g. To check the effect of different variables, such as starting volume of the container, vaporizing the reagents before exposing the samples, and others, smaller frames were made (fig. 3). The wire frames were stainless steel screen wire of such size that two of them could fit into the same size bag and be separated by a removable wooden clamp. In this way the reagents could be placed in one section and the sample in the other with other reagents if wanted. At any convenient time the clamp can be removed to achieve a variety of unusual conditions. Because only 4 g. or less of solution was found necessary in these small containers, the triple beam balance shown was set up so that the glass fabric which was permanently fastened to the wire frame could be suspended on the balance and weighed to an accuracy of about two hundredths (0.02) of a gram while spraying. Also, with these small frames a flat piece of the screen wire was used to hold the samples so that they could be easily inserted into the frames and not shift while the bag was being carried and sealed.

The sample size used for most runs in the large frame involved single layers of print cloth, 8 x 10 inches and weighing 5.4 g. several were made by using four layers and one run involved two pieces, 10 x 37 inches, weighing 25 g. each, and rolled into two separate rolls about 1 inch in

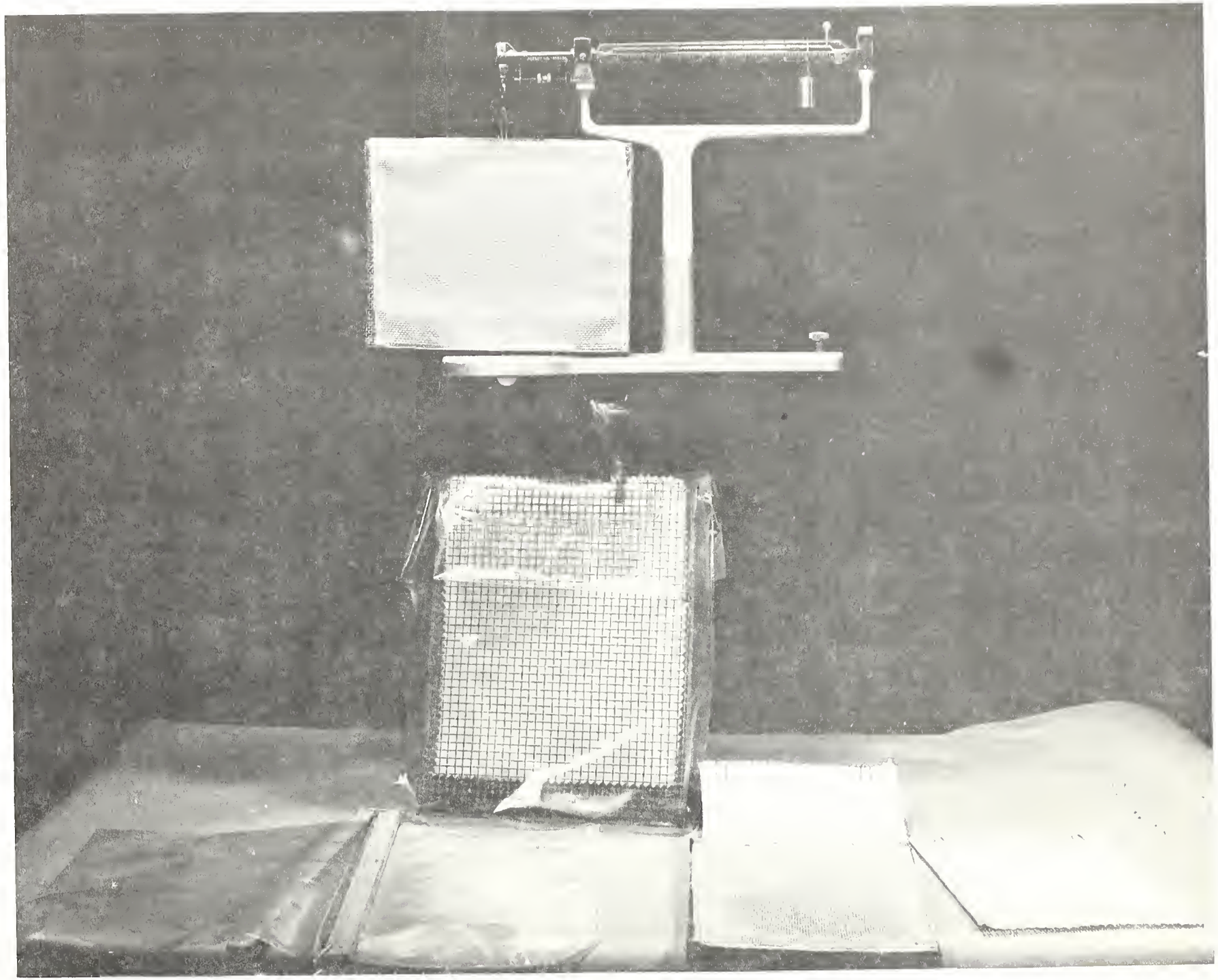

Figure 3. — Technique used to achieve uniform temperatures.

diameter by 10 inches long. The runs in the small frame utilized samples that were 8 x 37 inches, weighing 20 g., but folded and pressed to give six layers measuring 8 x 6+ inches. Several runs were made using two and three of these 20 g. samples.

The composition of the liquid reagent used in the runs is as follows:

	Percent
CH_2O	26.7
SO_2	27.6
CH_3OH	7.2
H_2O	38.5

This is the reagent that will be referred to as FSO_2 subsequently. The F meaning formalin, not fluorine. For comparison, water at room temperature will absorb only about 6 percent SO_2. This mixture is very close to the saturation point. The reagent was prepared by bubbling gas from a cylinder into 37 percent formalin while stirring and cooling. The composition was calculated from the weight increase. The reagent is quite stable. It has a boiling point of about 72° C. A similar solution made with paraformaldehyde to eliminate the methanol reacts equally as well but is not quite as stable. If methyl formcel is used, a large amount of precipitate forms overnight.

Figure 4 is a view of the plastic bag in the oven after heating about 5 minutes.

Figure 5 shows the reaction rate curves obtained at 200° F. using various amounts of the liquid reagent plus one series in which 2 g. of it were diluted with 2 g. of 37 percent formalin, effectively increasing the formaldehyde concentration and decreasing the SO_2.

Figure 6 is a plot of wrinkle recovery versus percent bound CH_2O. The parameter is the amount of liquid reagent used but the points comprising each curve were obtained time-wise. These curves indicate that a given wrinkle recovery can be obtained at various reagent concentrations, but note the order. The 3 g. runs produce a given wrinkle recovery at the lowest value of bound formaldehyde. In other words, there is a reversal between the 2- and 4-gram concentrations. Also, note that short curve at the top of the 2 + 2 curve. Actually, it is labeled as 2 + 2 but it is really the results obtained with 2 + 1 and 2 + 1.5 grams of FSO_2+ formalin, respectively, both at 30 minutes reaction time. This is an interesting trend which certainly requires further investigation. The reversal between 2 and 4 g. of FSO_2 is more evident in figure 7.

This is what might be called wrinkle recovery angle rate curves. This is not the rate at which a given sample recovers in the Monsanto tester, but rather the standard test values obtained on the same samples shown in figure 6, but plotted against time rather than percent bound formaldehyde. The parameter is the same as previously. Here the reversal in the rate of wrinkle recovery test value as the amount of reagent is varied between 2 and 4 g. is quite evident at reaction times of less than 20 minutes. But above this time we begin to get a more normal situation. This trend also merits further investigation.

A plot of percent breaking strength retained in the warp direction versus the percent bound formaldehyde is shown in figure 8. All of the samples whose properties were shown in the previous graphs are represented in the cross-hatched area. There were no distinct separations with respect to changes in the conditions of the systems, therefore, no separate line curves could be drawn.

In connection with breaking strength, if percent retention in the filling direction had been plotted instead of warp values, an area of similar size would have resulted but it would have been displaced downward about 10 percentage units.

These results indicate that this closed, relatively constant pressure, expandable container system is quite applicable to the cross-linking of cotton fabric with formaldehyde. Also, the properties obtained are generally comparable with those obtainable with conventional cross-linking resins. Although large-scale reactions on garments have not been conducted, it does seem feasible. Also, as the title of this paper states, it is proposed that the oven used to heat the container could well be an existing garment curing oven. This proposal, of course, could well be premature because it is based on the reactions

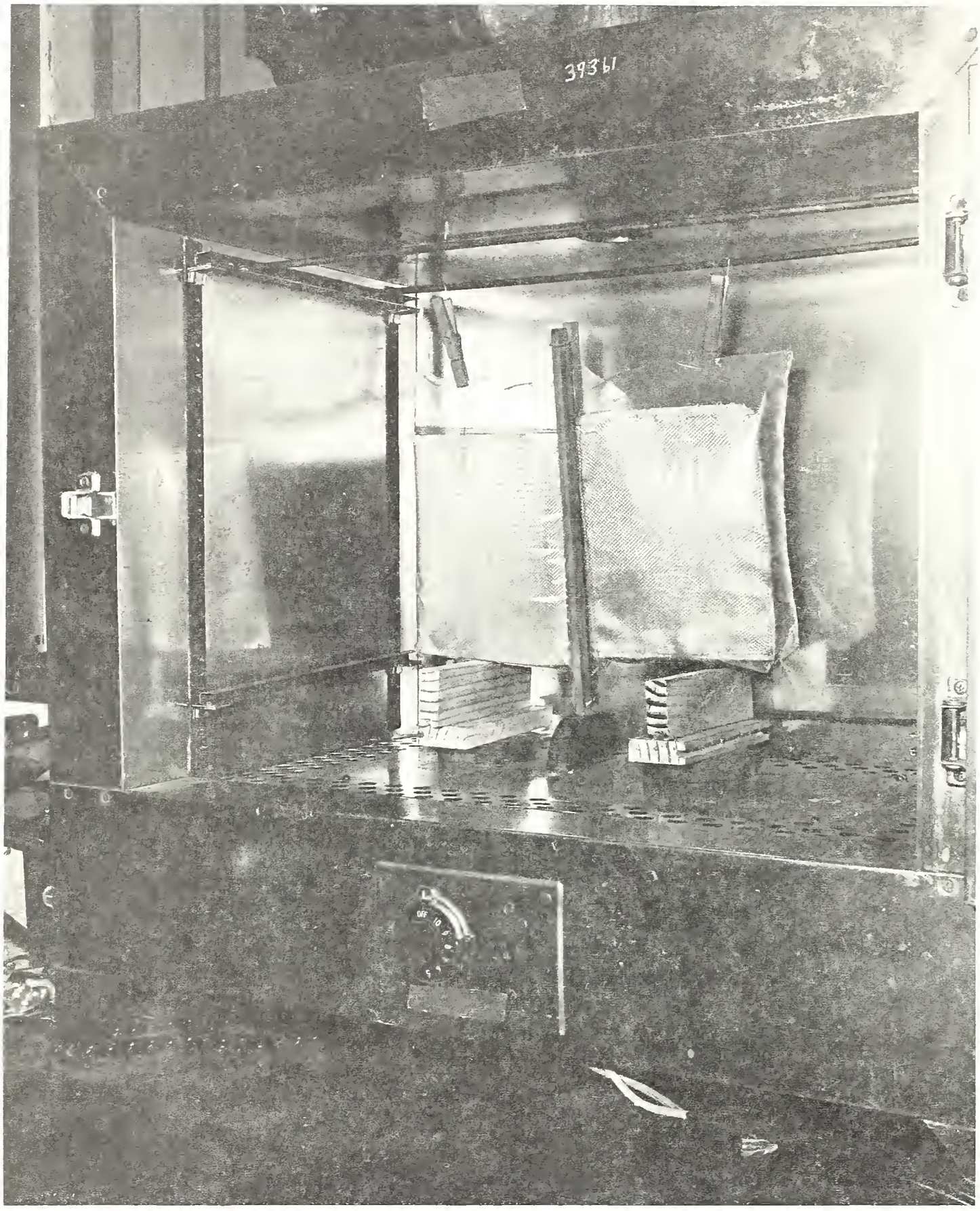

Figure 4. — View of plastic bag in oven.

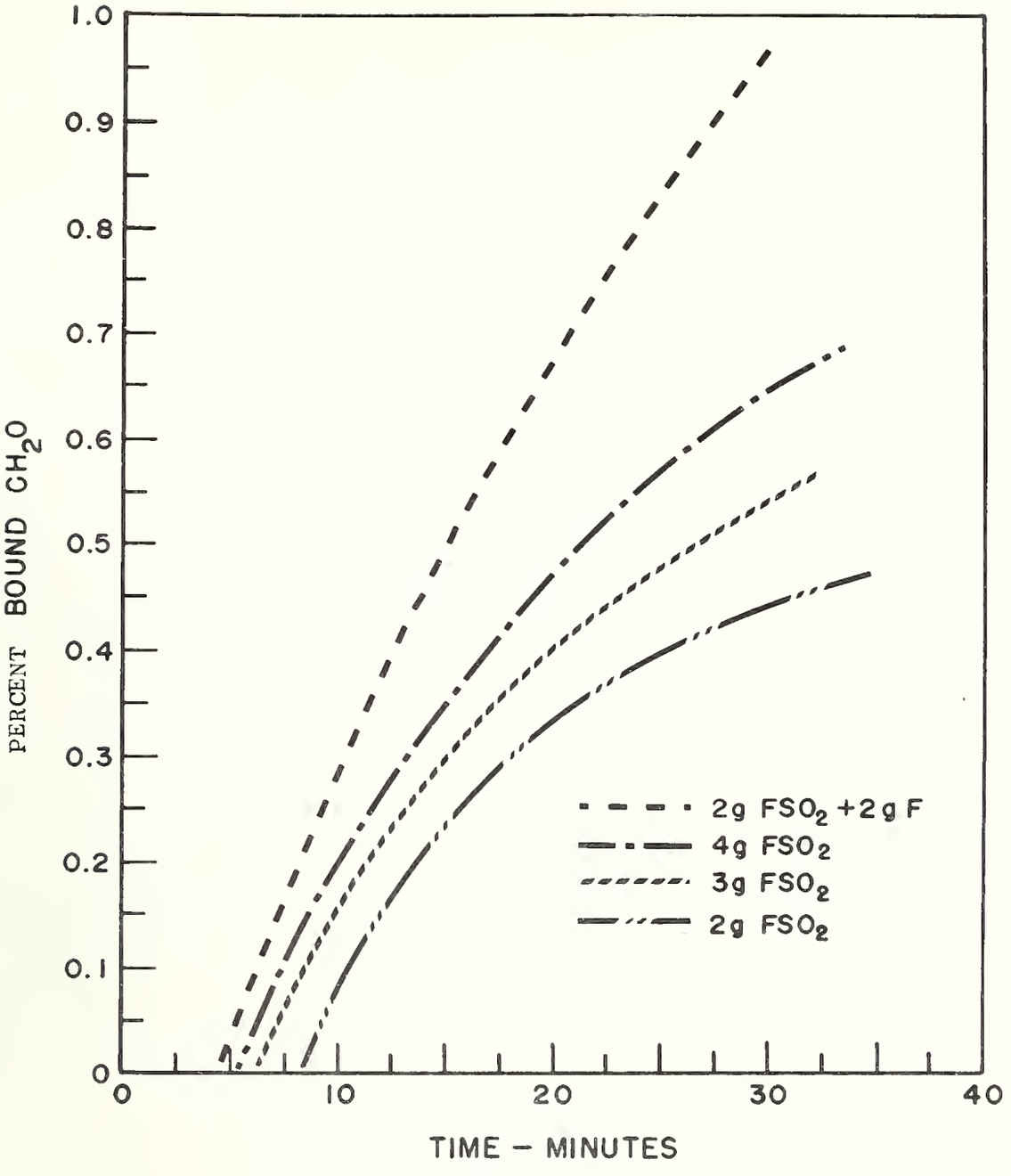

Figure 5. — Reaction rate curves at 200° F.

and properties obtained and not on such economic factors as the cost of containers, ventilation equipment at the entrance and exit points, excess space occupied in the oven, and many others. These economic factors could well defeat the commercial application. In which case, the ace in the hole might be the use of the technique as a laboratory tool.

But, assuming that the proposal was commercially feasible, the following data would aid in scaling up to full size cotton garments.

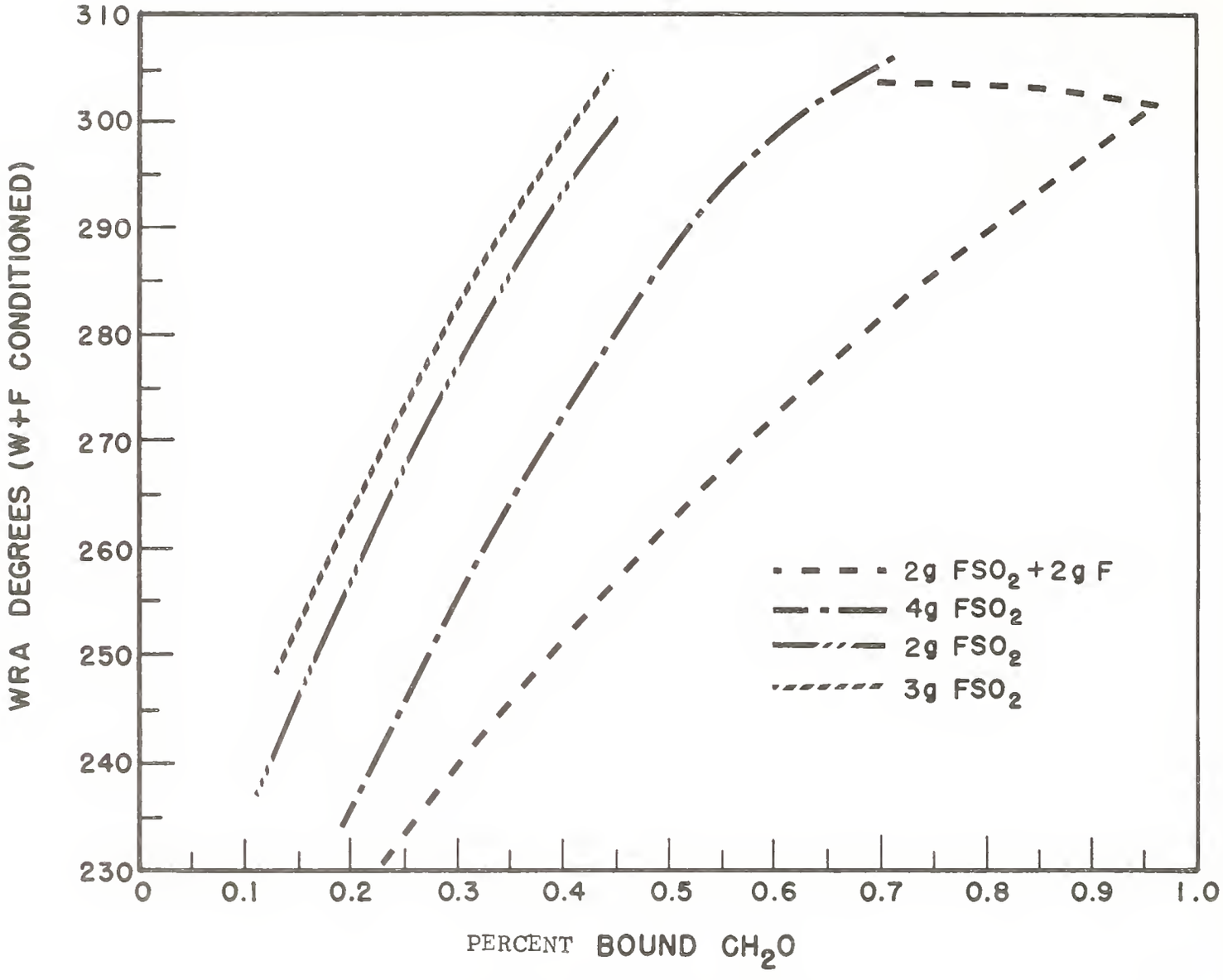

Figure 6. — Plot of wrinkle recovery versus percent bound CH_2O.

Figure 9 is a plot of percent bound CH_2O versus the molar ratio of SO_2 to formaldehyde in the reagents for a reaction time of 30 minutes at 200° F. The parameter here is Mols. of SO_2 per liter of starting volume. The short lines represent runs that were made at the constant ratio of the stock FSO_2 solution, except the one displaced to the right which was made by diluting the FSO_2 solution with sulfurous acid. These short lines also represent runs made at two levels of starting volume. The long curve represents the run in which the FSO_2 solution was diluted with formalin, along with comparable runs using only the FSO_2 solution. It seems feasible to assume that these curves should reach a peak somewhere in the upper left and then decrease to the origin. Further, investigations to determine the position of these peaks is indicated.

A plot of percent bound formaldehyde versus the weight of cotton in the system is presented in figure 10. We found the parameter in this case to be the molar concentration of the formaldehyde based also on the starting volume of the container. These curves are based on the same

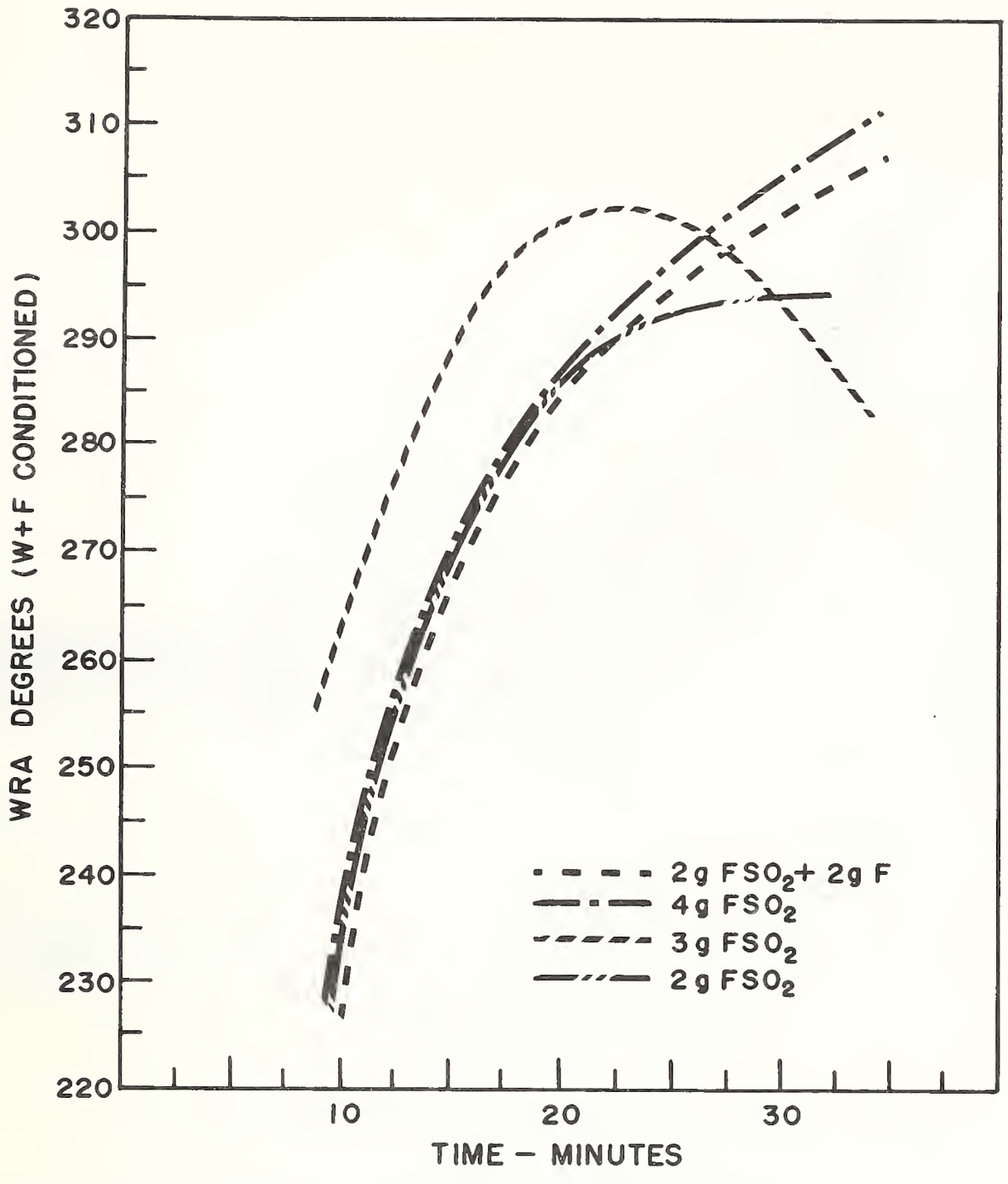

Figure 7. — Wrinkle recovery angle rate curves.

runs in the previous figure and, therefore, are a mixture of two starting volumes, several levels of cotton in each volume and, of course, the variation of the reagents used. Here again, the trends are strong but a few more corroborating runs are in order before scaleup conclusions can be made with confidence.

There is another part of the system, as used, that needs defining because variations in its physical characteristics will affect the results. That part is the vaporizing surface, as shown in table 2.

The title here says surface area, but there is more involved than that. In all of the other runs a single layer of glass fabric approximately the same size as the projected area of the cotton sample was used. The first line of the table is such a run. The next three runs were made by

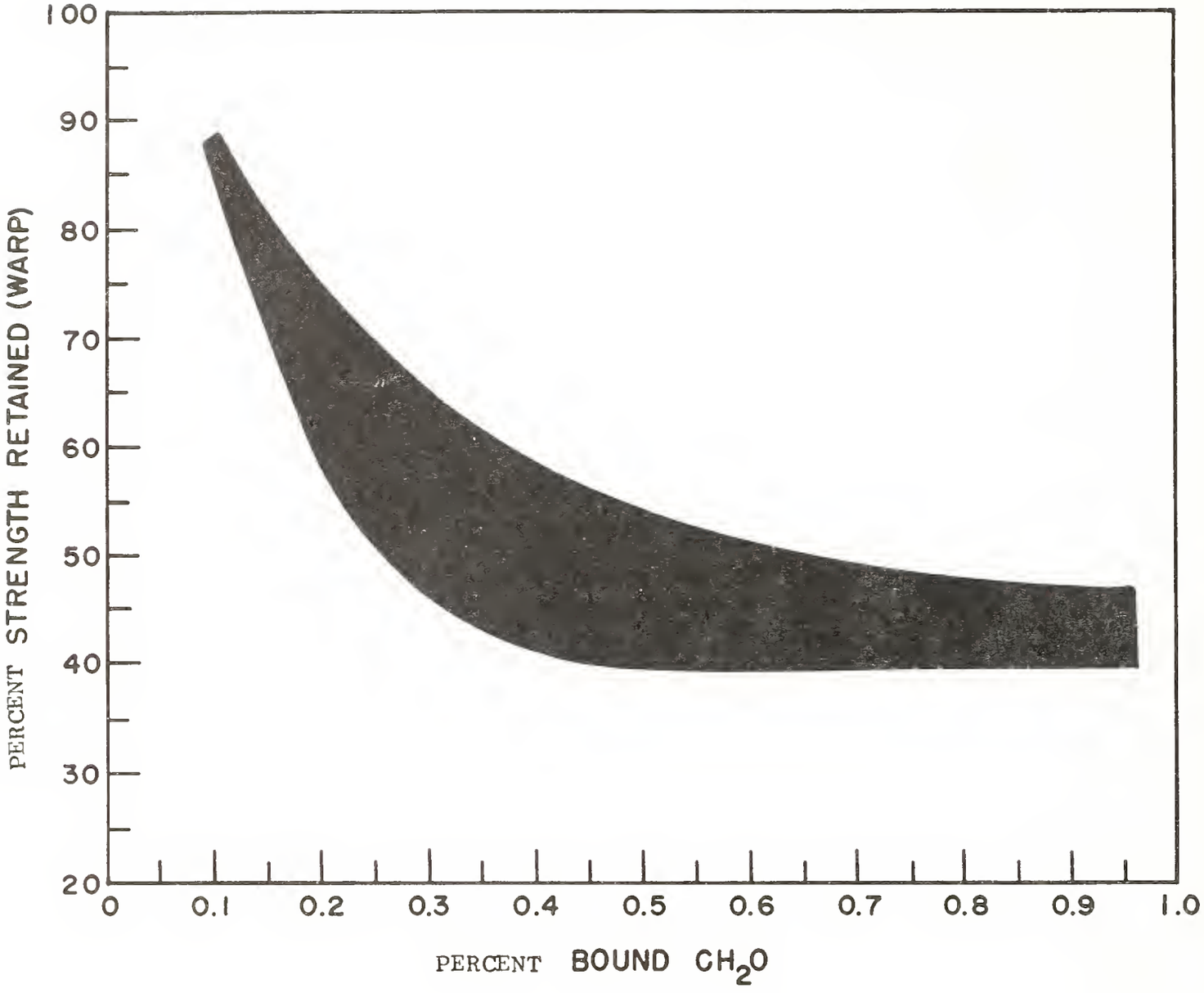

Figure 8. — Plot of percent breaking strength retained in warp direction versus percent bound formaldehyde.

cutting the glass cloth in half and laying the two halves on each other. This was necessary to maintain a constant amount of reagent without exceeding the saturation point of the glass fabric. The results obtained are not necessarily owing to the reduced projected area but could reflect the effect owing to reduced heat transfer caused by the additional thickness.

Several other factors were noted and must be mentioned. One is apparent diffusion of vapors through the low density polyethylene bags that were used. There is evidence that it exists but the amount has not yet been determined. Another is the extreme reactivity of this FSO_2 reagent towards cotton. That is, the liquid at elevated temperatures readily degrades cotton. A third factor is the moisture relationships in the system. Only laboratory equilibrated samples have been used thus far.

The data obtained in a comparative study of various reagents specifically directed to cross-linking cotton with formaldehyde in what might be called a conventional, open, constant volume system have been summarized. Although certain

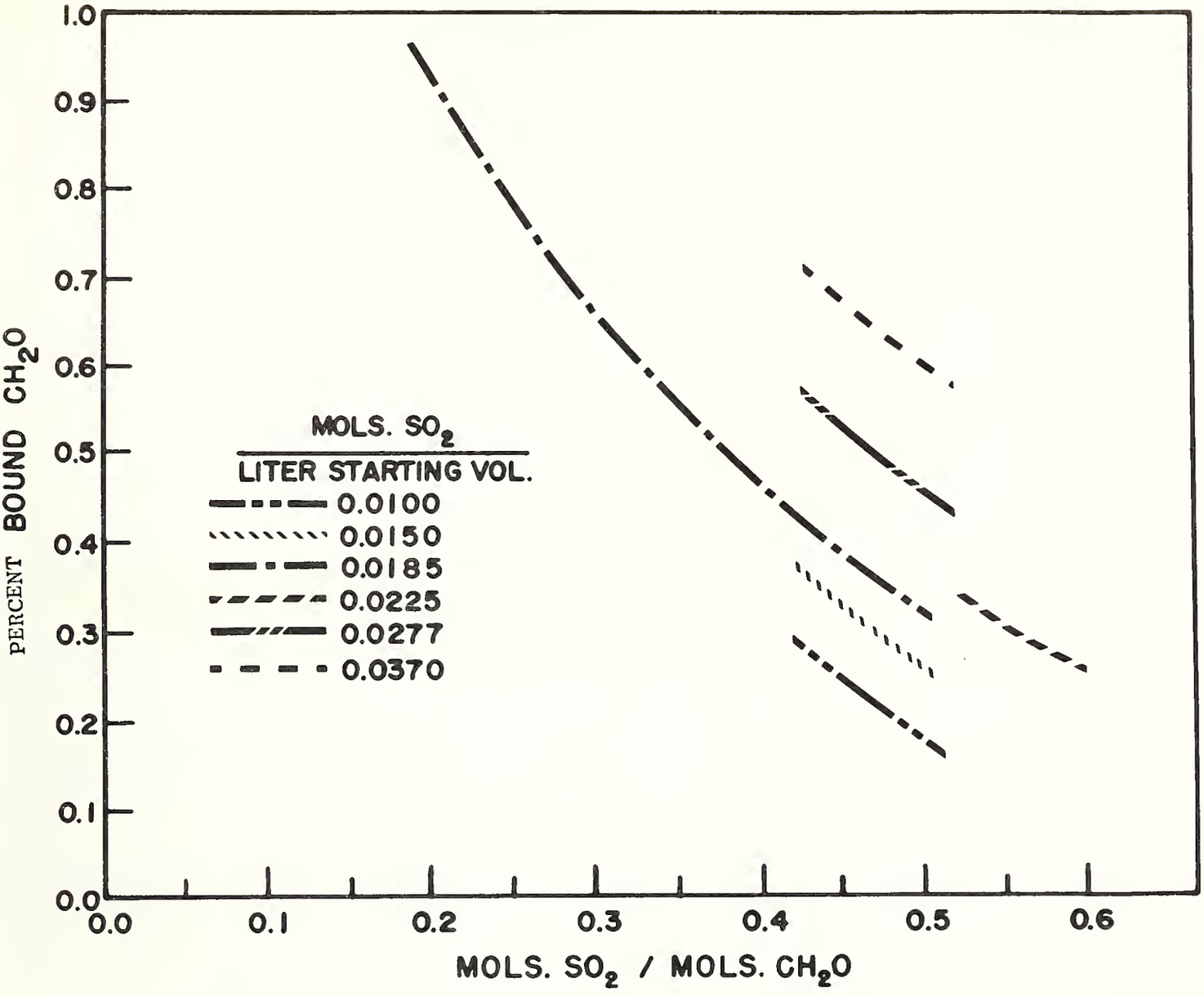

Figure 9. — Plot of percent bound CH_2O versus molar ratio of SO_2 to formaldehyde in reagents for reaction time of 30 minutes at 200° F.

conclusions were reached from the data, it was evident that a knowledgeable analysis of the system was not readily possible. Accordingly, a novel system was devised which utilized a closed relatively constant pressure, container having a thin wall to aid heat transfer, an excess of wall area in the form of folds or pleats to minimize pressure buildup, and heated externally in an oven. In addition, the system utilized an extended surface within the container to achieve rapid vaporization of the reagents.

Although additional work is necessary before a final, complete and confident analysis is possible which will allow scaleup to commercial size, the trends in reaction rates and final properties indicate that products comparable to those obtained by use of n-methylol type resins are feasible. This may seem like a dubious advantage but possible economics and the use of existing curing ovens instead of special vapor phase reaction chambers could inagurate some vapor phase treatments that would increase the utilization of cotton.

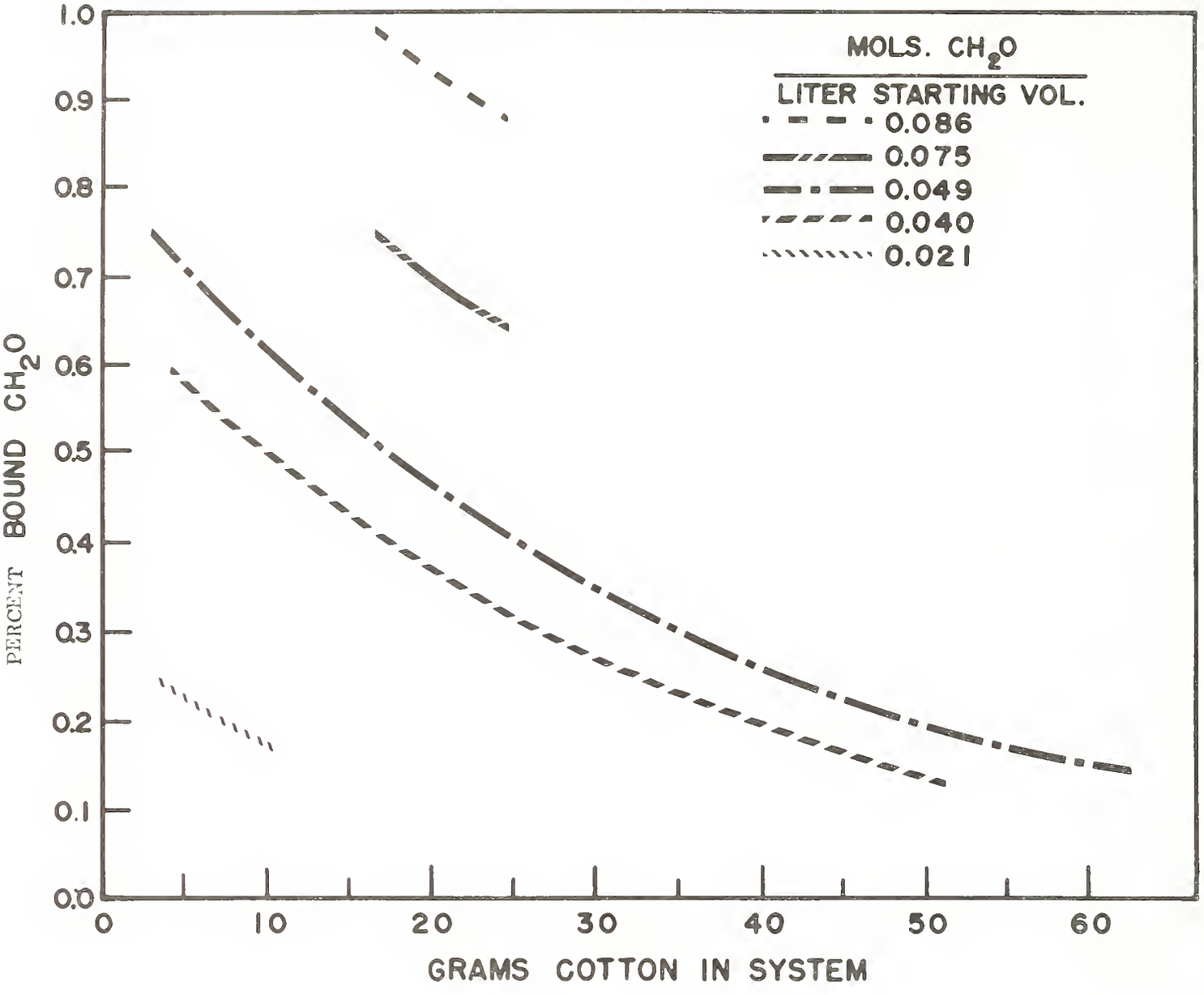

Figure 10. — Plot of percent bound formaldehyde versus weight of cotton in system.

Table 3. — Vaporizing surface area[1] versus properties

Glass cloth size	Number of layers	Pct. Bound CH_2O	WRA (W+F) cond.
8x10	1	0.49	266
4x10	2	.41	275
4x5	4	.26	266
4x2.5	8	.18	235

[1] 8g. FSO_2, 30 min., 200°F., 5.4g. cotton.

CARBAMATE AGENTS WITH LOW FORMALDEHYDE RELEASE FOR POST-CURE DURABLE PRESS

by

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(Presented by J. David Reid)

This is a preliminary report of progress in a study of formaldehyde release from cotton fabrics that have been sensitized by treatment with carbamate finishing agents for post-cure durable-press (DP) processing.

Carbamate finishing agents were introduced in 1961 (2). Since that time they have gained general commercial acceptance for the pre-cure finishing of white durable-press cottons. There is presently some usage of carbamate finishing agents for post-cure durable-press processing. However, a considerable increase could be realized if the formaldehyde-release characteristics of the sensitized fabric could be improved. Carbamate-treated cottons enjoy several advantages over post-cured fabrics that are finished with presently used agents. Among the advantages of carbamate finishes are (a) the durability of the finish to removal by hydrolysis in laundering, (b) the resistance of the finish to chlorine damage, (c) the reduced tendency of the fabric to yellow on curing, and (d) amenability of the agent to compounding with soil release agents for single bath application. These advantages have contributed to the great popularity of carbamates for white durable-press items.

The use of carbamates for post-cure DP has been severely limited because of their high release of formaldehyde from sensitized fabrics during the storage and manufacturing period. The objective of this work was to develop a carbamate finishing agent that is more suitable for use in post-cure DP.

Before proceeding, certain terms must be defined. Free formaldehyde is the formaldehyde which is unreacted and is, therefore, free to evaporate from the sensitized cloth and cause trouble. Bound formaldehyde is the nonvolatile formaldehyde which is held as part of the methylolated crosslinking agent or by some other means. Sensitized fabric is material which has been impregnated with a methylol crosslinking agent and catalyst, and treated at a temperature sufficient to dry the fabric without causing any substantial amount of reaction of the agent with cellulose. The sensitized cloth can then be fabricated into a garment, creased and shaped as desired, and then cured to make this configuration durable for the life of the garment.

Formaldehyde release can be attributed to two phenomena, free formaldehyde present after sensitization and formaldehyde subsequently freed by decomposition of the methylolated agent. The present paper deals primarily with the former. A future paper will discuss formaldehyde release from agent decomposition in greater detail.

Unfortunately, there are few guidelines to define a satisfactory product; that is, a sensitized fabric satisfactory to the nose of the garment manufacturer. However, the AATCC (1) has suggested that 300 p.p.m. (0.03 percent) of formaldehyde on the weight of the goods is not detectible by the nose whereas 3,500 p.p.m. (0.35 percent) is highly odoriferous and objectionable.

There is a second standard which may be used. This is to make comparisons with those commercial preparations that have achieved acceptance by the garment makers. From personal communications with industrial finishers, it was ascertained that 1 percent or less free formaldehyde is considered satisfactory in commercial 45 to 50 percent solutions. When several commercial dimethylol dihydroxyethyleneurea preparations—the agent generally used

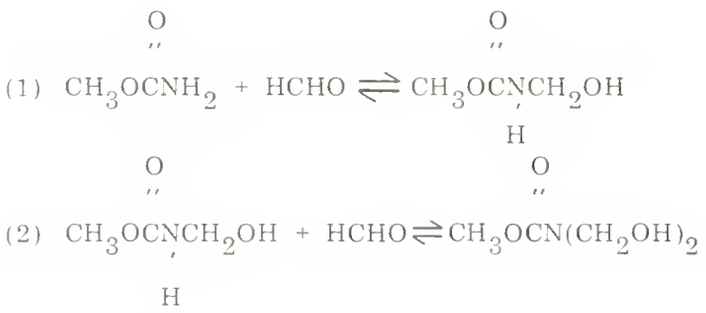
for post-cure—were examined, about 0.8 percent or less free formaldehyde was found in the 45 to 50 percent solutions. Lately some carbamates have been offered as low formaldehyde carbamates and these were found to have from 0.3 to 1.5 percent free formaldehyde. Examination of these indicated that nitrogenous agents other than carbamates had been added, presumably to react with free formaldehyde. However, some of these carbamate agents were not entirely satisfactory. In table 1 are summarized the data obtained on the free formaldehyde content of some commercial agents.

Table 1. — Free formaldehyde content of various commercial finishing agents

Commercial agent	Free HCHO [1]
	Percent
Dimethylolcarbamates	4.2, 5.4
Dimethylol carbamates (special, low HCH0)	1.6, 0.6, 0.3
Dimethylol dihydroxyethyleneurea	0.6, 0.7, 0.9
Dimethylol ethyleneurea	1.9
Dimethylol propyleneurea	6.7
Dimethylol substituted propyleneurea	3.7
Dimethoxymethyl uron	2.1

[1] Determined by the sulfite titration method.

In the first step of the methylolation reaction to prepare the finishing agent, methyl carbamate reacts rapidly and almost quantitatively with formaldehyde as shown in Equation 1, under high alkaline conditions such as pH 10. However, the second formaldehyde goes on slowly and with difficulty, Equation 2. The cross-linking agent is in equilibrium with the formaldehyde.



This is illustrated in figure 1 which shows that one mole of HCHO reacts almost quantitatively, but that when two moles are present, only 1.5 moles of formaldehyde have reacted. Only half the carbamate is present as the dimethylol derivative and thus, only half is readily available for cross-linking. Also, this means that a half-mole of free formaldehyde is present. To push the equilibrium a little further, it is customary to use 2.2 to 2.5 moles of HCHO in the preparation of the agent. There will be about 6 percent free formaldehyde in a 50 percent solution of the agent. These results are not peculiar to carbamates as all of the common nitrogenous agents are in similar equilibrium states with formaldehyde. Although the carbamates are in equilibrium as shown at the high pH at which they are made, carbamate agents are stable for years when the reacting medium is adjusted to a near neutral pH. Therefore, if a carbamate agent can be produced with low free formaldehyde, it should remain that way during the storage period.

It must be considered whether excess free formaldehyde in the finishing solution will be left on the sensitized (padded and dried) cloth or whether large amounts of this formaldehyde might volatilize during drying. This question is answered by figure 2 which shows the percentage of free formaldehyde on fabric when methyl carbamate agents with various molar ratios of formaldehyde to carbamate are applied. Fabrics treated with the usual methyl carbamate preparations all fall in the area between "satisfactory" and "objectionable;" that is, they are intermediate in their degree of acceptability. However, it is obvious that a high formaldehyde-content preparation cannot be used with the hope that the excess formaldehyde will volatilize during ordinary drying.

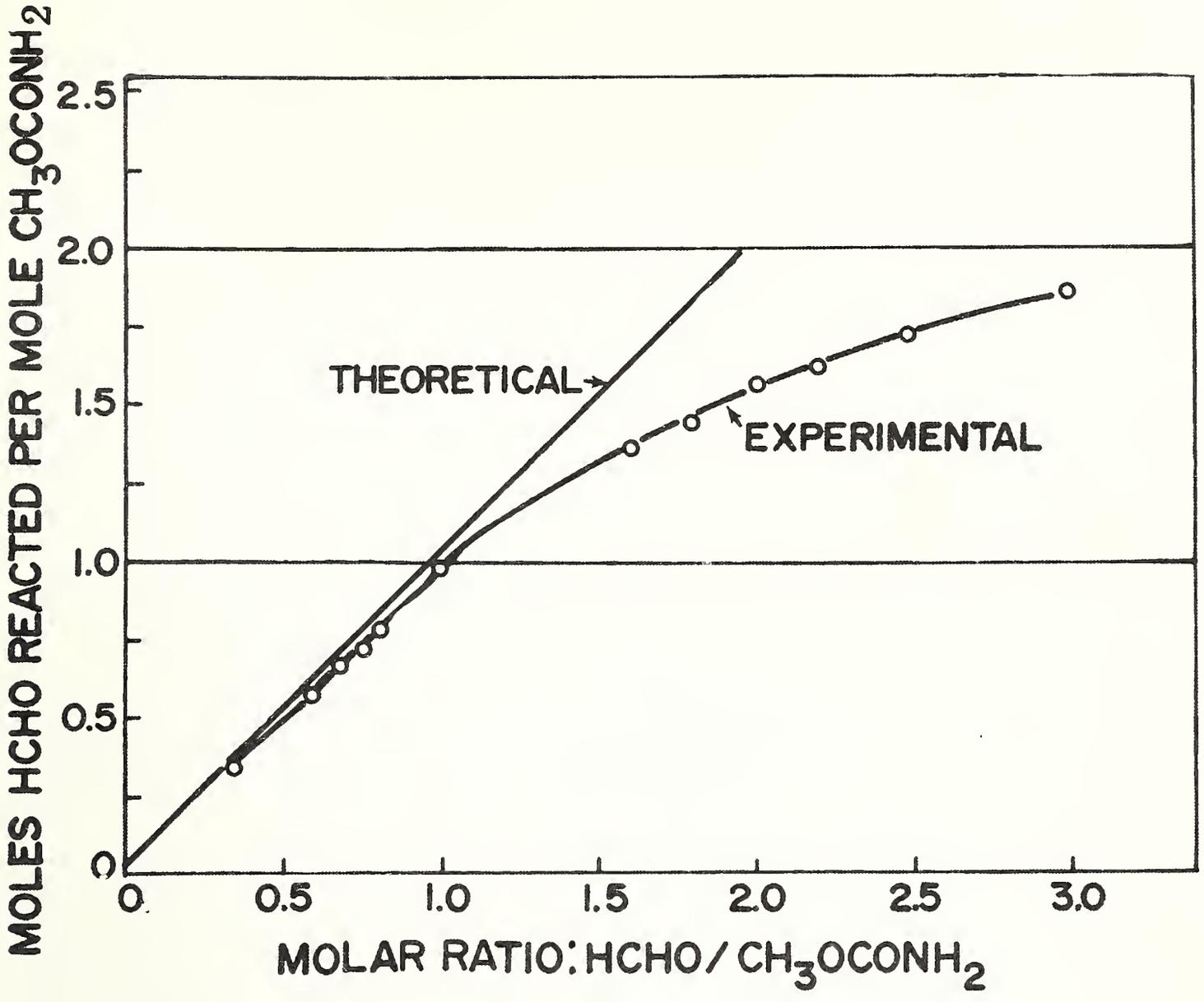


Figure 1.— Extent of reaction between formaldehyde and methyl carbamate (MC) as a function of the molar ratios of the reactants.

Thus, to summarize to this point, the free formaldehyde content of sensitized cloth will be a function of the amount of formaldehyde retained during the drying period plus what may be formed during the storage period minus what may escape during the storage period.

Three general methods of producing carbamate finishing solutions with less free formaldehyde are possible. One of these is to make a reaction product with better efficiency of reaction. Another is to remove or destroy the excess formaldehyde by physical means, and a third is to react the excess formaldehyde with something which will reduce free formaldehyde without harm to the finish.

It is not possible in the presentation to describe all the variations that were investigated. However, dimethylol methyl carbamate (DMMC) was synthesized by a recently disclosed method (7) in which methyl carbamate is fused with paraformaldehyde. This was an improvement over the usual aqueous preparation for decreased free formaldehyde content. However, the reduction in free formaldehyde was only

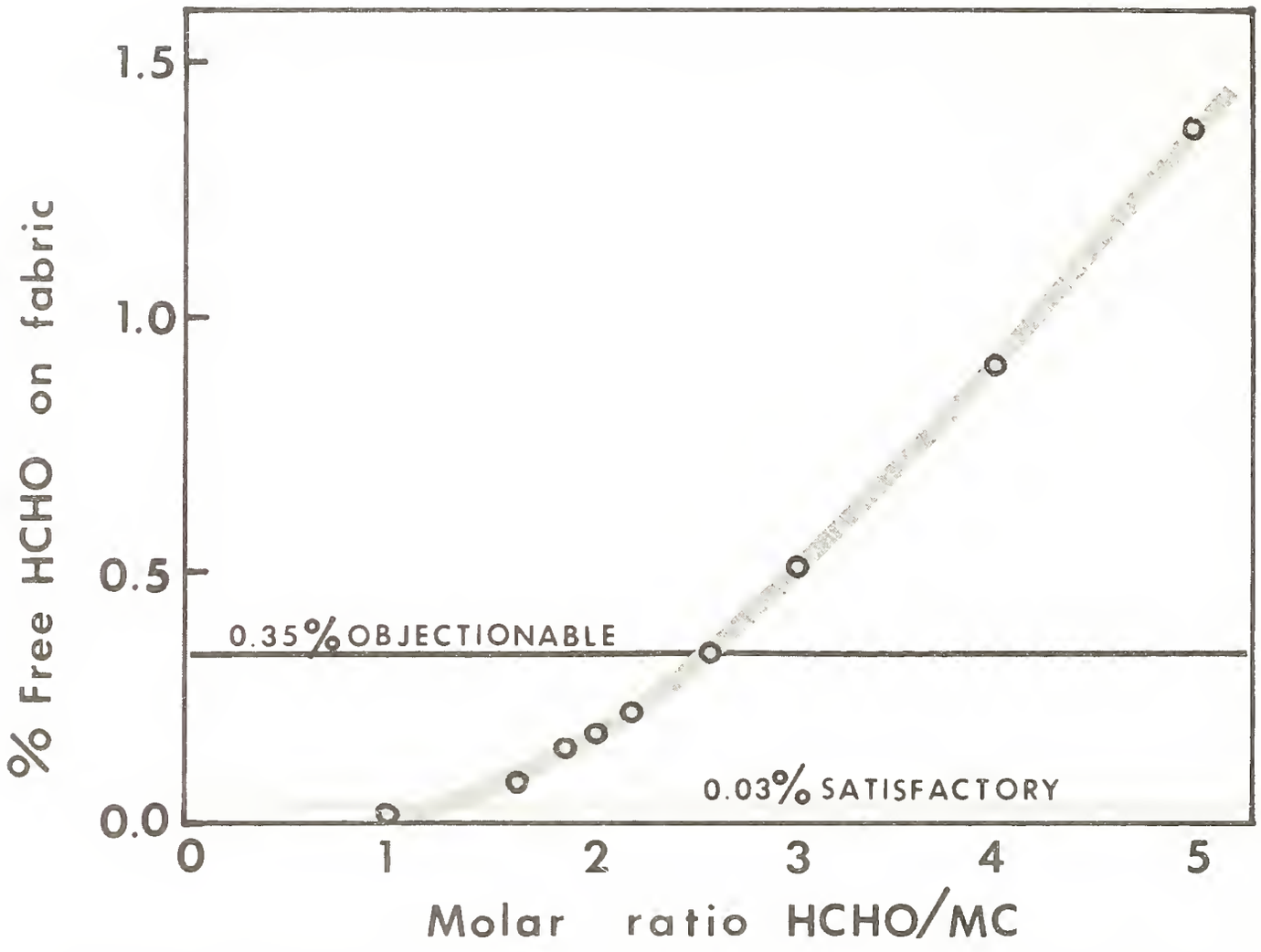


Figure 2. -- Free formaldehyde on sensitized fabric from treatment with 10 percent methyl carbamate-formaldehyde adducts prepared from various molar ratio of reactants.

from 4.4 percent for the conventional aqueous methylolation of 2.4 percent for the fused product.

Attempts to remove free formaldehyde from 50 percent DMMC solutions by distillation and other physical methods were not successful.

Attention was turned, therefore, to the reaction of the free formaldehyde with something which would form a stable compound. It is known that dimethylol carbamates are quite stable in the pH range of 5 to 8 (5). Within this pH range, it should be possible to react the free formaldehyde with an active compound without disturbing the equilibrium.

The first compound tried was sodium sulfite. In the determination of free formaldehyde, the formaldehyde is reacted with sodium sulfite at low temperature to produce the sodium formaldehyde-bisulfite addition product:

$$HCHO + Na_2SO_3 + H_2O \longrightarrow HOCH_2 \cdot NaSO_3 + NaOH$$

By this reaction the free formaldehyde in a 50 percent DMMC solution was reduced from 6 percent to a little more than 1 percent. When the unmodified DMMC solution was applied to cloth and dried, the cloth had a free formaldehyde content of 0.2 percent and a readily detectable odor of formaldehyde. The sulfite-modified DMMC solution produced a fabric with little odor and 0.07 percent free formaldehyde. When these fabrics were cured (magnesium chloride catalyst), both had dry wrinkle recoveries of 250° to 260°. However, in the chlorination-scorch test, the modified fabric suffered a 30-percent loss in strength.

Attention was then turned to reaction of the free formaldehyde with other agents which are used in cross-linking, such as ethyleneurea, propyleneurea, or triazone. The idea, of course, was that if the excess formaldehyde could be used to dimethylolate something such as propyleneurea, a mixed cross-linking agent would result with utilization of the formaldehyde. Some of the agents tried and the results obtained are listed in table 2.

Table 2. — Decrease in free formaldehyde content of 50 percent dimethylol methyl carbamate solution by modification with various agents

Modification agent [1/]	Free HCHO
	Percent
None (DMMC, 2.2:1)	5.9
Ethyleneurea	.1
N-Methyl ethyleneurea	1.2
Dihydroxyethyleneurea	4.5
5-OH Propyleneurea	4.7
Hydroxyethyl triazone	5.2

[1/] Mole of agent used per mole of free formaldehyde.

Of those listed, only ethyleneurea and N-methyl ethyleneurea were used successfully. Furthermore, these agents were added on the basis of one mole of agent for each mole of formaldehyde which would mean that the added material was not useful in cross-linking. Indeed, the monomethylol ethyleneurea could cause chlorine damage on bleaching. The N-methyl ethyleneurea would not cause chlorine damage but it is an expensive compound and would not seem to be practical. It was particularly disappointing not to get reaction with propyleneurea because theoretically (6) the monomethylol agent would not lead to chlorine damage. However, the work of Petersen (4) offers an explanation of why it did not react like ethyleneurea. Petersen has shown that while ethyleneurea is reactive with formaldehyde at almost any pH, the rate of reaction of propyleneurea with formaldehyde is so slow between pH 3 and 9, that for all practical purposes, there is no reaction.

Table 3 shows that the ethyleneurea-modified carbamate agents give wrinkle-recovery angles equal to the unmodified solution and these angles are durable both to acid hydrolysis at pH 3.2 and to stringent alkaline laundering. The ethyleneurea causes the finish to be susceptible to chlorine damage. Thus, ethyleneurea-modified carbamates yield solutions with practically no free formaldehyde but the fabrics so treated can be damaged by chlorine bleaching after stringent laundering. Therefore, these agents would be useful mainly on colored fabrics which would not be bleached or on white polyester/cotton blends where chlorine damage is not as great a consideration as it is with all-cotton fabrics.

Another approach to the development of a formaldehyde-free fabric is that of removing the free formaldehyde from the sensitized fabric. The remainder of this paper presents some early findings from this area of research. A laboratory technique for aeration of sensitized fabric is promising for removal of free formaldehyde.

In previous work it was noted that formaldehyde is held tenaciously by cotton when it is absolutely dry (3). However, if the dry fabric is allowed to pick up moisture from the atmosphere, the formaldehyde is displaced by the water. In plant practice, sensitized fabric is fairly dry and the rolls are immediately sealed in polyethylene bags.

The effectiveness of aeration was demonstrated by the following experiment: Cotton fabric was padded with solutions of DMMC

Table 3. — Effect of ethyleneurea modification of dimethylol methyl carbamate on the properties and durability of the finished cotton

	DMMC-finished		EU mod.-DMMC finished	
	Wr. rec. angle (W+F)	Cl-scorch damage	Wr. rec. angle (W+F)	Cl-scorch damage
	Degree	Percent	Degree	Percent
Finished	270	4	273	0
Same, after hydrolysis at pH 3.2	270	2	259	64
Same, after 5 alkaline launderings	272	4	273	30

containing various contents of free formaldehyde (zinc nitrate catalyst) and dried. The sensitized fabrics were then exposed to air by hanging them up for 24 hours, all free formaldehyde disappeared as is shown in table 4. Great amounts of free formaldehyde can be removed by this technique. For example, a fabric which contained more than 5 percent free formaldehyde on the weight of the fabric when wet, contained 1.4 percent after the drying period, and no free formaldehyde at all after aeration.

Figure 3 shows the progressive loss in free formaldehyde from aeration of a fabric treated with a solution containing 10 percent DMMC and zinc nitrate catalyst. The pad bath contained about 1.25 percent free formaldehyde. After 8 hours aeration, the free formaldehyde was down to zero. Thus, if the fabric is aerated, finishing solutions with large amounts of free formaldehyde may be used.

The removal of free formaldehyde from sensitized cloth can be speeded up greatly by aeration with forced air. It would be possible then to remove free formaldehyde by passing sensitized cloth counter-current through a narrow chamber using high-speed, forced air with the proper moisture content. It might be better to perform this aeration at the garment plant to get rid of any formaldehyde that might be produced by decomposition of the agent on the cloth during storage.

Studies on the decomposition of DMMC on sensitized cloth carried out over a period of several months are not yet complete. However, the AATCC test (1) has been used to determine the evolution of formaldehyde from sensitized cloth treated with several finishing agents (table 5). Although this accelerated test may be too stringent, the results obtained do indicate that aeration and ethyleneurea modification decrease formaldehyde release from these sensitized fabrics. A comparison with the common post-cure finishing agent, dimethylol dihydroxyethyleneurea, also is provided in this table.

In summary, the free formaldehyde content of the usual commercial carbamate finishing agents is too high for them to be used for post-cure durable-press garments. It is possible to react the excess formaldehyde with agents, such as sodium sulfite or ethyleneurea, to yield a product with very low free formaldehyde. However, chlorine resistance is reduced in these two cases and these products would be more suitable for fabrics which are not intended to be bleached.

A simple laboratory method of preparing sensitized fabrics with low formaldehyde release is to aerate the fabric under forced draft with air containing sufficient moisture to displace the formaldehyde vapors.

Table 4. — Free formaldehyde content of fabric after padding, sensitizing, and aerating

Carbamate agent used molar ratio of HCHO/MC	Free HCHO in fabric		
	After padding	After sensitizing	After aerating
	Percent	Percent	Percent
2.0	0.92	0.17	0.00
2.2	1.14	.22	.00
2.5	1.45	.31	.00
3.0	2.29	.51	.02
5.0	5.08	1.36	.00

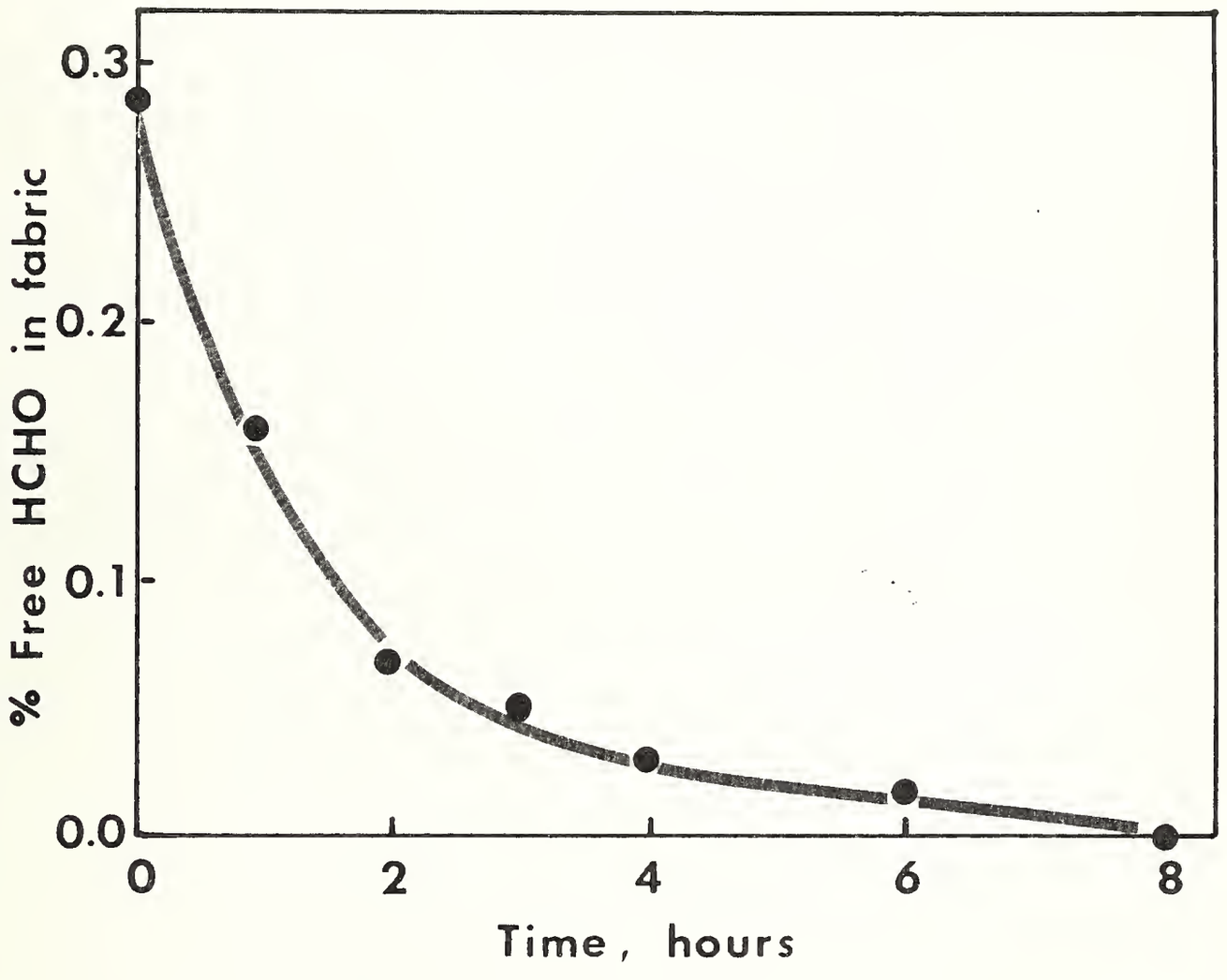


Figure 3. — Decrease in free formaldehyde in sensitized fabric by aeration.

Table 5. — Formaldehyde released from sensitized cottons in AATCC Test 112-1968

Finishing agent used	HCHO released
	Percent
Dimethylol methyl carbamate	0.5
Same — after aeration	.1
Same — ethyleneurea modified	.3
Commercial dimethylol dihydroxyethyleneurea	.8

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DISCUSSION

QUESTION: In the determination of free formaldehyde that you carried out, was this done on vapor, cloth, or by some other means?

DR. REID: The sulfite titration method was used on samples of the cloth.

QUESTION: Is this meaningful? What you determine quantitatively in an extract might not correspond to what's free in the cloth and what may evaporate in storage.

DR. REID: Determinations carried out on the cloth correspond very well with the odor tests carried out by smelling with the human nose. However, the AATCC test for formaldehyde odor (sealed jar test) seems to be too severe.

QUESTION: In the aeration proposed for removal of free formaldehyde, is there any tendency for the carbamate itself to evaporate?

DR. REID: Methylolated carbamates can decompose and sublime. However, in the relatively short times of aeration that are effective, one would not expect to lose a significant amount of carbamate. Methyl carbamate is the most volatile and it was used in the present work. Higher alkyl carbamates or substituted carbamates, such as hydroxyethyl carbamate, should not sublime at all. This has been demonstrated in some of our previous work.

FIFTH SESSION: R. Bruce LeBlanc, National Cotton Council of America, Memphis, Tenn., Chairman

INVESTIGATIONS IN THE STEAM CURING OF METHYLOL AMIDES ON COTTON

by

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(Presented by D.V. Parikh)

ABSTRACT

Moist-cure cross-linking treatments, producing (1) an unusual combination of high dry and high wet wrinkle recoveries, and (2) high wash-wear ratings after line drying, are in vogue in Europe. However, they have not been popular with the American textile industry because of their time consuming batchwise nature.

A continuous, or potentially continuous, steam-cure finish employing superheated steam that gives properties similar to those obtained by moist-cure treatments has been developed. The steam-cure finish offers some distinct advantages over the earlier processes because danger of fiber degradation is reduced. The need for a thorough neutralizing wash is eliminated, and enough latitude is provided for deviations in process conditions during commercial application. Furthermore, the finished fabric exhibits better strength retention than fabric finished by the conventional pad, dry, cure process.

The steam-cure procedure studied, employed steam-cure alone and steam-cure with a subsequent dry-cure. The former gave better results, but the latter was effective with a wider variety of agents.

The crosslinking of cellulose in a cotton fiber that contains 4 to 10 percent water is claimed to produce superior strength and a particularly effective combination of dry and wet wrinkle resistance in wash-wear or durable-press cotton. The process is known as "moist-cure" finishing. The procedures reported for moist-cure finishing use common finishing agents. However, they use mineral acid catalysts and require long reaction times at temperatures near 25° C. The process is, therefore, necessarily a bath process. To produce cotton fabric with similar properties by a process that uses a short reaction time and is potentially continuous, the curing of methylolamide cross-linking agents in superheated steam was investigated. In steam, cotton cannot be completely dried even at temperature well above 100° C. Therefore, the reaction of the finishing agent and cellulose occurs in a fiber with appreciable water content as it does in the moist-cure process.

EXPERIMENTAL AND RESULTS

For treatment of cotton fabric with steam curing in this investigation, common methylolamide finishing agents were used with a catalyst of equimolar proportions of magnesium chloride hexahydrate and citric acid. This catalyst was sufficiently active for use in steam at 100 to 140° C., without the hazards of mineral acids at elevated temperature.

An example of the results that can be obtained with steam curing is shown by the following treatment. Cotton printcloth was padded with a mixture of 20 percent dimethylol dihydroxyethyleneurea, 1.25 percent magnesium chloride - citric acid catalyst, 2 percent emulsified polyethylene, and 0.1 percent wetting agent. The padded fabric was run into a pilot-plant size flash-ager directly with superheated steam. The ager was typical of those used to fix prints but was operated to give the fabric dwell times of 10 minutes at 127° C. and 6 minutes at 138°C. The fabric was washed after steaming. Both fabrics were evaluated by standard tests, and the results compared with those obtained by conventional curing in dry heat using a standard formulation of the same agent. The comparison is shown below:

Curing conditions	Wrinkle recovery angles (degrees, W + F) conditioned wet at 65 pct. RH		Retention (pct. of original) resistance to Stoll flex abrasion	breaking strength	tear resistance	Moisture regain (pct.)
Steam at 127° C.	292	272	88	78	62	8.4
Steam at 138° C.	300	292	65	90	72	6.9
Conventional dry-cure	310	285	2	48	37	4.9

Curing in superheated steam clearly results in superior strength and abrasion resistance. The increase in wet wrinkle resistance from steam curing is less than expected although the high moisture regain indicates that the fibers have a greater swelling ability than those cross-linked conventionally in dry heat. The greater swelling ability is confirmed through examination of swelling behavior by microscopy. The high wrinkle recovery angles should give good durable-press properties. Unfortunately, for most of this work, the ager used in this work introduced wrinkles from uneven tension and water spots which precluded evaluation by the usual tests. Toward the end of this study, these difficulties were overcome in part, and it was found that satisfactory durable-press ratings (overhead lighting), approximately 4.0 for line drying or tumble drying could be obtained. These ratings probably can be improved.

Steam curing can also be used with fabric dried conventionally to a controlled moisture content before entering the steam chamber. This procedure will shorten the dwell time in the steam chamber because only curing and not drying and curing in steam will be required.

In addition to dimethylol dihydroxyethyleneurea, dimethylol methyl carbamate, and dimethylol ethyleneurea were also tried in a steam-cure process. These last two agents, in general, were more difficult to use. In a procedure similar to that described they produced wrinkle-recovery angles no higher than 260°.

A variation of the steam-use process was foundapplicable to a greater variety of methylolamide agents. This variation consists of a steam-cure followed by a dry-cure. The curing is not completed in steam.

After a partial cure in steam, curing is completed in dry heat but with a shorter time or lower temperature than used in conventional dry-cure processing. Typically such a procedure will use a formulation like that described previously and will use a steam-cure at 127° C. for 5 minutes followed by dry-heat at 100° C. for 3 minutes. The fabric properties obtained from this variation of the steam-cure process are intermediate between those from steam-cure alone and those from a conventional dry-cure. The variation however, can be used with a wider variety of agents. Dimethylol methylol carbamate, for instance, gives quite good results. It also may be usable in a wider variety of existing equipment.

The reason that steam curing gives higher strength at the same performance level is believed to be the formation of some reaction product in the wet cotton that is not formed in the conventional dry-cure process. In the combination of steam-curing and dry-curing, some agent reacts during the initial cure in steam. This agent is bound in the cotton, as indicated by nitrogen content after washing, but gives little increase in wrinkle resistance. However, the effect of this product persists through the subsequent dry-curing. Presumably this product is formed also when the steam-cure is the only cure.

SUMMARY

Curing of cross-linking agents in superheated steam offers a method of producing wrinkle-resistant cotton fabric with improved retention of strength and abrasion resistance and with increased moisture absorptivity. The high wrinkle resistance indicates that the process should be able to give durable-press performance. The process uses ordinary methylolamide finishing agents with a special catalyst. However, dimethylol dihydroxyethyleneurea seems the most suitable methylolamide agent for the process. In comparison with moist-curing, steam-curing offers a process that is potentially continuous, is

simple, has a wider latitude for variations in procedure, and presents less chemical hazard to workers, equipment, and fiber. The advantages result mainly from eliminating the mineral acid catalyst of the moist-cure process.

DISCUSSION

QUESTION: When the two step process, steam followed by dry curing, is employed can one get durable creases in post cure garments?

DR. D.V. PARIKH: This system is meant for pre-cure processes only. This is caused by the active catalyst system employed. Any length in time lapse between drying and curing operations would likely hydrolyze the finishing agent on the sensitized fabric. Further research will be needed to adapt the process for DP.

QUESTION: Please repeat the concentration of mixed catalyst used.

DR. D.V. PARIKH: A $MgCl_2$ $6H_2O$ to citric acid ratio of 1:1 was employed. In steam curing 20 percent finishing agent was used with 1.25 to 1.5 percent mixed catalyst.

The conditions used for the control printcloth sample treated by the pad-dry-cure technique were requested. These were: drying 7 minutes at 60° C, curing 3 minutes at 160° C.

QUESTION: What would happen to printcloth if the finishing agent-catalyst system used for steam curing were dried 6 minutes in an oven as in pad-dry-cure at 280° F. with no steaming?

DR. D.V. PARIKH: This was not the proper control for comparison. The aim of the current work was to obtain a moisture finish on a continuous basis and the steam-cure process has achieved a better fabric than is now achieved in a normal pad-dry-cure process.

QUESTION: Can you attribute the good strength properties to steam or to the mixed catalyst system used? What would happen if the mixed catalyst was used with 120° C. curing temperature?

DR. D.V. PARIKH: The aim of the present steam-cure work is to improve the European process and such a comparison is, therefore, not considered.

COMMENT: In steaming the atmosphere contains 100 percent moisture and the fabric will retain 4 to 6 percent moisture after being exposed to steam curing, whereas 120° C. in an oven would remove all moisture. Consequently, one would get different fabric properties.

QUESTION: How is the width controlled in cross-linking being achieved in the steamer?

DR. D.V. PARIKH: The fill width is not controlled in the flash ager, but such controls could probably enhance smooth drying performances.

A DURABLE FLAME RETARDANT FINISH FOR COTTON USING CYANAMIDE-THPC RESINS

by

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(Presented by F. L. Normand)

ABSTRACT

A new flame retardant finish for cotton based on the reaction product of THPC with cyanamide in the presence of phosphoric acid was developed. Cotton fabrics were padded with a 25 to 36 percent total solid solution containing a 2:1 molar ratio of cyanamide to THPC and 2.0 to 2.5 percent phosphoric acid to give about 80 percent wet pickup. Curing temperatures ranged from 140° to 160° C., 8.5 oz. Sateen having an 8.5-percent add-on, and a 3.2 oz. printcloth having a 15-percent add-on passed the standard vertical flame test after 30-laundering cycles. This finish was successfully applied in a pilot plant scale. Treated fabrics had a good hand and appearance. Losses in breaking strength and tearing strength were of the same order of magnitude as for wash-wear fabrics. Chlorine bleaching alone did not visibly discolor any of the treated fabrics. There was a very slight yellowing after chlorine bleaching and scorching. The finished fabric did not exhibit ion exchange properties.

INTRODUCTION

A flame-retardant finish based on cyanamide-phosphoric acid has been known for a number of years (3, 5, 9). Because of the commercial availability of an economical, relatively stable aqueous solution of cyanamide, interest has been renewed in this flame retardant. O'Brien (6) has recently reported on a cyanamide-phosphoric acid flame-retardant finish for cotton. His findings show that the degree of durability depends on the concentration of the reactants and on the hardness of the wash water.

Several flame-retardant finishes developed at the Southern Regional Research Laboratory are based on tetrakis (hydroxymethyl)phosphonium cloride, THPC (4). These THPC-based polymers can be easily applied to cotton fabrics to impart a very durable flame-resistant finish.

Therefore, it was theorized that by incorporating a durable flame retardant like THPC, in the cyanamide phosphoric acid formulation, a reaction would occur between the THPC and the cyanamide. Hopefully this new finish would improve the durability and strength properties of the cyanamide treated fabrics.

This paper describes a new THPC flame-retardant finish for both light and heavyweight cotton fabrics. The finish is based on the reaction product of THPC with cyanamide and phosphoric acid. When the treated fabrics are ignited, little odor or smoke is observed; in fact little odor is noted throughout the entire processing of the fabric.

Materials and Methods

Fabric description.--Two cotton fabrics were used: a desized, scoured, and bleached 80 x 80 printcloth (3.2 oz./sq.yd.), and a desized scoured, and bleached cotton carded Sateen (8.5 oz./sq.yd.).

Chemicals used.--The THPC used in this work was a crystalline product of high purity obtained from Hooker Chemical Company. The cyanamide used was a 50 percent aqueous solution obtained from the American Cyanamid Company. The phosphoric acid was reagent grade (85.6 percent) obtained from J. T. Baker Company.

Processing procedure.--Fabric samples were padded through the treating solutions, using two dips and two nips with a squeeze roll pressure adjusted to obtain 70 percent wet pickup for the

sateen fabric and 85 percent wet pickup for printcloth.

The treated fabric was dried in a forced draft oven for 5 minutes at 85° C. and cured at 140° to 160° for 2 to 10 minutes. The fabrics were then rinsed in running tapwater and dried. Application of Triton X-400 as a softener can be used as an aftertreatment or added to the treating solution.

Test methods.--All physical testing was performed by standard methods under standard conditions of 70° F. and 65 percent relative humidity; breaking strength, 1-inch-strip method (2a); tearing strength. Elmendorf method (2b); crease recovery, Monsanto method (2c) and flame resistance, standard verticle method (8).

Phosphorus was determined by the colorimetric reduced molybdate method after digestion with sulfuric acid and perchloric acid (7). Damage due to retained chlorine was determined by treating the fabrics with sodium hypochlorite solution, rinsing, drying, pressing between hot metal plates, and then measuring the breaking strength (1).

Durability of the finish to laundering was determined by repeated washing of the treated fabric in an agitator-type home machine under normal washing conditions for cotton using a commercial detergent.

Experimental and Discussion

Preliminary experiments indicated that a flame retardant polymer could be made by polymerizing cyanamide and THPC with phosphoric acid. Since this polymer was flame resistant and insoluble in water, studies were carried out to determine its usefulness as flame-retardant finish for cotton. Studies were conducted to determine the optimum mole ratio of cyanamide to THPC, amount of resin add-on, and curing temperature for imparting durable flame resistance to cotton fabrics.

Effect of mole ratio to cyanamide to THPC upon resin add-on and physical properties of the fabric.--White sateen samples were treated with 36 percent total solids solutions containing 1:2, 1:1, 2:1, and 3:1 mole ratios of cyanamide to THPC and 2.5 percent phosphoric acid. Resin add-ons of the treated fabrics were comparable when the mole ratio of cyanamide to THPC was 1:1, 2:1, or 3:1. Lower resin add-on was obtained when the fabric was treated with the 1:2 mole ratio of cyanamide to THPC. Percent add-ons ranged from 9.3 percent for the 1:2 mole ratio of cyanamide to THPC to 16.3 percent for the 3:1 mole ratio. The char lengths ranged from 2.5 to 3.0 inches at the higher add-ons to 3.5 inches for the lowest add-on. After 30 laundering cycles all fabrics passed the standard critical flame test with char lengths of 2.0 to 3.0 inches.

Fabrics treated with 1:1 or 1:2 mole ratio of cyanamide to THPC were very weak, and retained 26 to 40 percent of their breaking strength; fabrics treated with 3:1 or 2:1 mole ratio retained 75 percent of their breaking strength. However, fabrics treated with the 3:1 mole ratio were yellow. Therefore, it was decided the 2:1 mole ratio cyanamide to THPC would be used in subsequent formulations.

Effect of cure temperature on resin add-on and tear strength.--Sateen and printcloth samples were treated with aqueous solutions containing a 2:1 mole ratio of cyanamide-THPC. The phosphoric acid content was 2.0 percent in a 25 percent total solids solution for sateen, and 2.0 percent phosphoric acid content in a 30 percent total solids solution for printcloth. Increasing the curing temperature from 140° to 150° C. increased the resin add-on for sateen and reduced the curing time from 10 to 5 minutes. A comparable high add-on (11 percent) was achieved when a higher cure temperature (160° C.) was used with a shorter cure time (3 minutes). The tearing strength retention (47 to 53 percent) and breaking strength retention (38 to 40 percent) of the fabrics were lowest for fabrics when cured at the highest temperature. Similar results were found for the printcloth. The breaking and tearing strength of the print cloth were decreased as the cure temperature was increased. The breaking strength retention ranged from 56 to 69 percent and the tearing strength retention from 56 to 62 percent. Increasing the cure temperature from 140° to 160° C. and decreasing the cure time from 10 to 2 minutes did not significantly increase the add-on.

The durability of the treated fabrics was not affected by varying the curing temperature from 140° to 160° C. After 30 launderings, the char lengths of the treated fabrics were 3.75 inches or less, and the phosphorus content of the treated fabrics decreased only 10 to 20 percent. The phosphorus retained was highest at 160° C.

Effect of phosphoric acid concentration on resin add-on, flame resistance, and tearing strength.--Cyanamide-THPC formulations containing various concentrations of phosphoric acid were applied to both the sateen and the printcloth to determine the effect of the acid on add-on, flame resistance, and strength of the fabrics. A 25 percent total solids solution was used for the sateen; a 30 percent total solids solution was used for the printcloth. The phosphoric acid content ranged from 1.5 to 5.0 percent. The treated fabrics were dried, and the printcloth was cured at 160° C. for 2 minutes, the sateen, at 150° C. for 5 minutes.

The resin add-on of the sateen fabric remained about the same with increasing phosphoric acid concentration. However, as the phosphoric acid concentration was increased from 1.5 to 5.0 percent both the breaking strength (62 percent) and tear strength (50 percent) were reduced to about 35 percent retention. The treated fabrics passed the standard vertical flame test and had char lengths from 2.8 to 3.8 inches. Therefore, a phosphoric acid concentration of about 1.5 to 2.5 percent appears preferable for the sateen.

Increasing the acid concentration from 1.5 to 5.0 percent increased the resin add-on on the printcloth, but the char length remained about the same (3.0 to 3.5 inches). The breaking strength retention of the treated samples was about the same (55 percent), but the tearing strength retention decreased from 54 to 44 percent as the acid concentration increased from 1.5 to 5.0 percent. Therefore, a 2.0 percent acid concentration again appeared optimum for good flame retardancy and good physical properties.

Several pieces of sateen were treated with a 30 percent solids solution with a 2:1 mole ratio of cyanamide to THPC and no phosphoric acid. The finish was not durable to laundering. It appears, therefore, that the presence of phosphoric acid, or a similar strong acid, is necessary in the formulation in order to impart flame resistance to fabric which is durable to repeated laundering.

Minimum amount of flame retardant needed in the treated fabric.--Samples of cotton fabrics were treated with solutions of varying concentration to ascertain the minimum add-on needed for initial flame retardancy and for durability to home laundering. Sateen and printcloth were treated with 2:1 mole ratio of cyanamide to THPC, dried, and then cured for 5 minutes at 150°, for sateen and at 140° C. for printcloth. Treated printcloth containing as little as 11.9 percent resin add-on passed the standard vertical flame test before washing, but after only five launderings, the fabric failed to pass the test. However, samples having about 15.2 percent resin add-on passed the flame test, and were still flame resistant after 30 launderings (char length 3.2 inches).

The sateen containing 7.6 percent resin passed the flame test and was durable to five launderings. About 8.4 percent add-on or more was needed on the sateen to pass the flame test after 30 launderings.

Effect of chlorine bleach and scorch on untreated and treated sateen fabric.--The samples treated with a 36 percent total solids containing a 2:1 mole ratio of cyanamide to THPC and 2.5 percent phosphoric acid were tested for damage due to retained chlorine.

Three samples of fabric were tested: an untreated control, a treated sample cured at 140° C. for 10 minutes (15.0 percent add-on), and a treated sample cured at 150° for 5 minutes (14.9 percent add-on). The sample cured at 140° possessed 75-percent strength retention while the one cured at 150° possessed 65-percent retention, as compared with the untreated control. The samples were bleached, scorched, and then laundered 20 times.

There was only a slight difference between the breaking strength loss for the untreated control and that of the treated samples after bleaching and scorching. After 20 washing cycles, none of the fabrics lost any significant amount of their breaking strength. Chlorine bleaching alone did not discolor the treated fabrics, as shown from reflectance

measurements; however, some very slight yellowing was observed after bleaching and scorching.

Pilot Plant

Two pilot-plant applications were made on printcloth. Samples 10 yards long and 18 inches wide were padded through a solution containing 8.5 percent cyanamide, 19.5 percent THPC (2:1 mole ratio) and 2.0 percent phosphoric acid. Two dips and two nips were used to a wet pickup of 88 percent. The treated fabrics were dried for 2 minutes at 85° C. and then cured at 150° on the tenter frame, one sample for 4-1/2 minutes and the other for 2-1/2 minutes. Unreacted resin was removed by washing in a winch for 15 minutes in hot water followed by 15 minutes in cold water. After drying on a tenter frame, the fabric was softened by padding it through a 4 percent solution of Triton X-400 to a 50 percent wet pickup and dried again.

Resin add-on increased for fabrics cured for the longer time, reflecting a slightly better efficiency. Both treated samples passed the vertical flame test before laundering and had char lengths of 4.0 inches; after 30 laundering cycles the char lengths were 4.0 to 5.0 inches. The treated fabrics retained about 50 percent of their original tearing strength and about 58 percent of their original breaking strength. The hand of the fabric was good. Ion exchange values of the treated fabrics were too low to be significant. Treated fabric with 16.7 percent add-on showed a 90° improvement in dry crease recovery and a 97° improvement in wet crease recovery as compared with untreated control. In addition, the treated fabric with 16.7 percent add-on showed a wash-wear rating of three after 10 launderings.

Throughout the entire pilot-plant operation there was hardly any detectable odor. Also, noteworthy was the fact that when a flame was applied to the treated fabric, only a small amount of smoke was given off with very little disagreeable odor. This property of the flame-retardant fabric might be of benefit in situations where, because of confined areas, fumes could be harmful or fatal.

SUMMARY

A new, durable flame-retardant finish for cotton, based upon THPC, and cyanamide with phosphoric acid, has been developed. Fabric was treated by padding it through a water solution of the three components, then drying and curing at elevated temperatures. The flame-retardant formulation imparts a high degree of flame resistance to sateen and printcloth fabric.

Sateen with as little as 8 percent add-on, passed the standard vertical flame test after 30 laundering cycles. About 15 percent add-on was required for printcloth to have this durability. Treated fabrics have a good hand and appearance. Losses in breaking and tearing strength associated with this treatment were about 25 percent and 50 percent, respectively. Chlorine bleaching alone did not discolor any of the treated fabrics. There was very slight yellowing after chlorine bleaching and scorching. The flame-retardant finish did not impart any color to the fabric and when treated samples were exposed to a flame very little odor or smoke was produced. This important property might be of benefit where fumes are harmful or fatal.

ACKNOWLEDGMENTS

The authors wish to thank L. Williams and M. J. Hoffman for assistance in the pilot-plant applications; to M. K. Smith and L. N. Bosworth for the textile tests, and to J. S. Mason for phosphorus analyses.

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DISCUSSION

QUESTION: What was the final pH of your standard solution and why did the fabric retain so much of its strength?

MR. NORMAND: The final pH of the treating solution was below 1, or very acidic. The fabric retained about 52 percent of its tearing strength and about 75 percent of its breaking strength. This degree of strength retention may be due to the low levels of phosphoric acid in the formulation.

QUESTION: Were the fabrics subjected to further launderings 40 or 50 and were they evaluated?

MR. NORMAND: The treated fabrics were subjected to 30 launderings and then laundering was discontinued. From the data obtained on the treated samples, we believe that the treated samples which were durable for 30 launderings probably will be durable for 40 and 50 launderings.

COMMENT: Flame retardancy may be related to the type of nitrogen left after washings.

MR. NORMAND: Your point is well taken. As a matter of fact, two types of nitrogen were found in the cyanamide-phosphoric finish as reported by O'Brien. We intend to investigate our cyanamide-THPC-phosphoric acid along these same lines.

QUESTION: Was there ion exchange with this type of finish?

MR. NORMAND: We ran ion exchange tests on treated fabric and found only insignificant amounts of ion exchange, indicating no appreciable amount of cationic nitrogen which is base exchangeable.

QUESTION: What was the P-N ratio? Why do you get better char lengths after 10 launderings? What is significant about the fact that a difference of 2.5 percent brings about durability to washing?

MR. NORMAND: We are still in the process of determining analytical data. We have some phosphorus analysis data but as yet no nitrogen data. In the near future we plan to have nitrogen analysis done. Then we will have values to determine P-N ratios.

Length of char is not a good measure of flame resistance. The fact that two treated fabrics (having comparable char length after five washings) have different char length after 10 washings (one sample BEL, the other a char length of 2.5 in.) indicates that the more durable sample is less effected by launderings.

A well-known fact in dealing with flame retardant finishes is that a certain minimum amount of flame retardant material must be present in or on the fabric to lower the decomposition temperature of that fabric, and thus prevent its burning when the flame is removed. Now if this certain minimum is not present, then the decomposition temperature of the fabric is not lowered enough to prevent its being consumed by flames.

FLAME RETARDANT COTTONS USING PHOSPHORUS-CONTANING TRIAZINES

by

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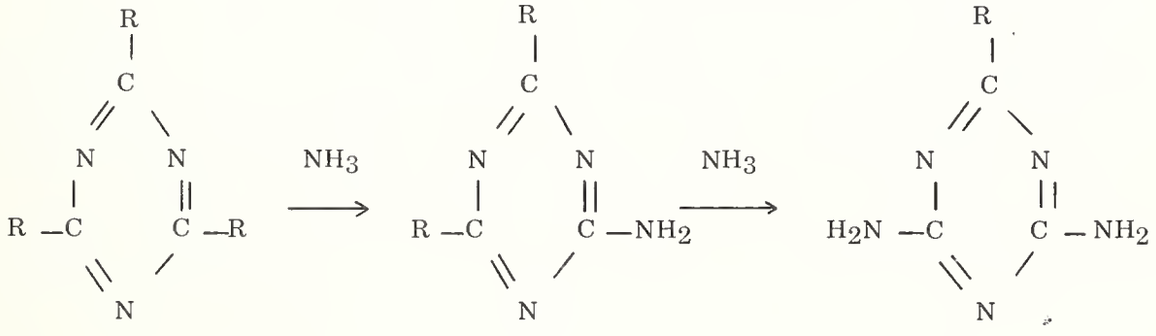
(Presented by J. P. Moreau)

The synergistic effect of phorphorus and nitrogen is known to impart good flame-retardant properties to cellulose (5). Therefore, an investigation of the preparation of phosphorus-containing triazines and their evaluation as possible flame-retardant finishes for cotton was initiated. Two such compounds evaluated were 2-amino-4,6-bisdiethoxyphosphinyl-1,3,5-triazine (ADPT) and 2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine (DAPT).

ADPT was easily prepared by the Arbusov reaction of monoaminodichlorotriazine with triethyl phosphite. Attempts to prepare DAPT by the same method, in which diaminochlorotriazine was reacted with triethyl phosphite, were unsuccessful. DAPT was, therefore, prepared by a new method as shown in the equation:



R = P(0) $(OEt)_2$ ADPT DAPT

When this reaction was carried out in ethanol DAPT was obtained in over 80 percent yield. ADPT was also isolated from this reaction and identified. However, when this same reaction was carried out in benzene, ADPT was obtained as the major product (75 percent yield) and DAPT was obtained in only 17 percent yield.

Therefore, the above equation represents a new method of preparing ADPT as well as DAPT. Also, as is shown in the equation and as would be expected, DAPT can be prepared directly from ADPT in very good yields.

Experimental.--Triethyl phosphite and cyanuric chloride were obtained from organic chemical suppliers and purified before using.

2-Amino-4,6-dichloro-triazine and 2,4-diamino-6-chloro-triazine were prepared according to Thurston and others (6).

2,4,6-Trisdiethoxyphosphinyl-1,3,5-triazine was prepared according to Hewertson, Shaw, and Smith (4).

ADPT (2-amino-4,6-bisdiethoxyphosphinyl-1,3,5-triazine) was prepared according to D'Alelio (3). ADPT was also prepared by the method described for DAPT but using benzene as the solvent. A recrystallized sample had a m.p. of 104° to 105° C. and elemental analyses in agreement with theoretical values. IR and NMR spectra also confirmed the structure.

DAPT (2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine) was prepared as follows: The trisdiethoxyphosphinyl triazine (0.20 moles) was dissolved in 400 ml. of absolute ethanol. The solution was cooled to approximately 0° C. then saturated with ammonia gas. The addition of ammonia was regulated so that the reaction temperature did not rise above 10° C. The solution was protected with a drying tube and allowed to stand at room temperature for at least 3 days. The precipitated white solid was removed by filtration, washed with water then acetone, and dried to give an 84 percent yield (0.17 moles). A sample was recrystallized from boiling water to give elemental analyses in close agreement with theoretical values. DAPT decomposed at approximately 275° C. IR and NMR spectra confirmed the structure.

TEXTILE TREATMENT

Materials and methods.--Desized, scoured, and bleached white sateen (8-1/2 oz.) was used for treatment.

Elmendorf tear strength (2a), breaking strength (2b), flex abrasion (2c), and wrinkle recovery (2d) were by standard ASTM procedures. Flame resistance was measured by the AATCC vertical flame test method (1).

A typical procedure for preparing an ADPT formulation consisted of: (1) refluxing ADPT in aqueous formaldehyde (mole ratio 1:2) for 30 minutes, (2) adding a softener (4 percent Velvetol OE) and wetting agent (0.1 percent Triton X-100), and (3) adding trimethylolmelamine (TMM) (mole ratio of TMM:ADPT of 2:1) previously dissolved in water, and (4) diluting to 40 percent reactive solids (total weight of ADPT, CH_2O, and TMM). The cotton sample was padded to approximately 80 percent wet pickup dried at 85° C. for 5 minutes and cured at 160° C. for 7 minutes. After a hot rinse and equilibration weight add-on was 20 percent.

The methylol derivative of DAPT was prepared by heating DAPT with aqueous formaldehyde (mole ratio 1:5) at 90° C. for 15 minutes. Softener and wetting agent was added as described above. The solution was diluted to 40 percent reactive solids (calculated as the tetramethylol derivative) then the pH adjusted with dilute NaOH to 6.6. The cotton sample was treated as described above to give a weight add-on of approximately 20 percent.

Results and discussion.--The strength properties of sateen treated by the ADPT formulation compared with an untreated control were reduced considerably as shown below.

ADPT - CH_2O - TMM

Sateen - 20 percent add-on

	Pct. loss	
	W	F
Abrasion resistance	89	66
Breaking strength	9	43
Tearing strength	38	62

The flame-resistance, wrinkle-recovery angle, and phosphorus-nitrogen analyses before and after five home launderings are:

ADPT - CH_2O - TMM

Sateen - 20 percent add-on

	Original	5 launderings
Char length, inches	2.7	4.1
WRA (W+F), degrees	281	279
P, percent	1.16	.86
N, percent	6.58	6.40

It shows that the ADPT-treated fabric passed the standard vertical flame test after five launderings and the wrinkle-recovery angle was virtually unchanged. Since practically no nitrogen was lost during laundering (<3 percent), it was assumed that the loss in phosphorus (26 percent) was caused by the bond breaking between the phosphorus and carbon on the triazine ring. Also, this cleavage of the phosphorus to carbon bond would produce an acidic material which could explain the strength loss properties.

The properties of sateen treated by the DAPT formulation at two different add-ons are given below.

DAPT-CH_2O treated sateen

	Add-on	
	19 pct.	15 pct.
Char length, inches	3.1	3.1
Abrasion resistance (F), percent	+100	+41
Breaking strength (F), percent	-22	-20
Tearing strength (F)	-40	-36
WRA (W+F), degrees	194	238

The flame resistance is very good even at 15 percent add-on. The strength properties are much better than those of the ADPT treated sample, particularly the abrasion resistance which was improved as much as 100 percent after treatment. Wrinkle recovery angle was increased only slightly.

The flame resistance, abrasion resistance, and phosphorus-nitrogen analyses before and after five home launderings are as follows:

DAPT-CH_2O treated sateen

	19 percent add-on		15 percent add-on	
	Orig.	5 Laund.	Orig.	5 Laund.
Char length, inches	3.1	3.2	3.1	3.2
Abrasion resistance (F), percent	+100	+68	+41	+77
P, percent	1.86	1.62	1.70	1.31
N, percent	4.00	3.36	3.46	2.57

There was no change in flame resistance after five launderings for both add-ons. The abrasion resistance also remained high compared with an untreated control. The percent loss in phosphorus was approximately the same as the percent loss in nitrogen. This indicated that the loss in phosphorus was caused by the loss in the polymer as a whole and not caused by cleavage of the phosphorus to carbon bond as in the case of ADPT. Breaking strength, tearing strength, and wrinkle recovery showed no significant change after five launderings. However, there was a noticeable improvement in the hand after only one laundering.

The flame-resistance and abrasion-resistance durability of the DAPT treatment at 20 percent add-on is given below.

DAPT - CH_2O

Sateen - 20 percent add-on

No. of launderings	Char length, inches	Abrasion resistance, percent
0	3.1	+100
5	3.2	+68
10	3.2	-6
15	3.0	-32
20	4.2	-30

The flame resistance of the treated sample was unchanged after 15 home launderings as indicated by char lengths, but began to show slightly less flame resistance after 20 launderings. Also, a sample subjected to a 3-hour soap-soda boil, burned the entire length as measured by the vertical flame test. The abrasion resistance decreased upon laundering when compared with the abrasion resistance of an unlaundered control. However, when compared with the respective laundered control, an increase in abrasion resistance was noted even after 20 launderings.

There were no significant changes in breaking strength or tearing strength after 20 launderings.

SUMMARY

ADPT (2-amino-4,6-bisdiethoxyphosphinyl-1,3,5-triazine) and DAPT (2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine) were prepared by a new method, that is, by the reaction of 2,4,6-trisdiethoxyphosphinyl-1,3,5-triazine with ammonia. ADPT was formulated with

formaldehyde and trimethylolmelamine and applied to 8-1/2 oz. white sateen to give good flame resistance and wrinkle recovery before and after five home launderings but with considerable loss in strength properties. The methylol derivative of DAPT was also applied to 8-1/2 oz. white sateen to give good flame resistance and abrasion resistance before and after 20 launderings. The loss in strength properties were comparable with those of a typical resin treated cotton fabric.

ACKNOWLEDGMENT

The authors are indebted to Textile Testing Investigations for physical tests, Ann Black for nitrogen analyses, Biagio Piccolo for phosphorus analyses, Nancy Morris and Elizabeth McCall for IR spectra, and Gordon Boudreaux for NMR spectra.

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DISCUSSION

QUESTION: Are the ethyl phosphate groups hydrolytically unstable? If so, are the ion-exchange properties the reason for the loss of flame retardancy on laundering?

MR. MOREAU: There is a possibility that we are getting some hydrolysis of the ester groups. We have not looked at the ion-exchange property of these compounds.

QUESTION: What are the effects of the treatment on odor and hand? Is there a formaldehyde odor on storage?

MR. MOREAU: The hand of the treated fabric is slightly stiffer than the control, bending moment is increased approximately six times that of the control. However, after laundering the bending moment of the treated sample approaches that of the control.

There is no odor to the fabric after treatment. There appears to be no problem with formaldehyde odor on the fabric upon storage.

QUESTION: Are the solutions stable?

MR. MOREAU: The ADPT solution is not stable longer than 3 hours because the solution becomes too acidic which polymerizes the trimethylolmelamine to give a white precipitate.

The DAPT solution appears to be stable for at least 1 month and possibly longer.

QUESTION: What is the explanation for the initial abrasion resistance and why does it drop after laundering?

MR. MOREAU: The increase in abrasion resistance, as explained to me by Dr. Vail, is due to the softener. A softener contributes greatly to increased abrasion resistance until the wrinkle-recovery angle approaches 270 degrees. At approximately 270 degrees the abrasion resistance begins to drop drastically.

FLAME-RETARDANT COTTON BATTING PRODUCTS [1/]

by

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(Presented by Paul A. Koenig)

Cotton batting is a cushioning material used in the bedding, automotive, and furniture industries. It is also known as felting, padding, or wadding. This product is a blend of various low grades of cotton fibers. Generally, it is composed of 60-percent first cut linters and 40-percent textile wastes. This ratio can vary depending upon economic considerations. The wastes include motes, fly, and sweeps. The blend of these fibers is processed by a garnett--which is the batting industry's equivalent to a coarse textile card. The fibers are discharged from the garnett in the form of a thin web of parallel fibers and then lapped to the desired thickness of cushioning material. This product is characterized by its softness and ability to absorb moisture and its general comfort qualities. However, it lacks substantial tensile strength and has poor resilience under conditions of high humidity.

Cotton batting holds about 60 percent of the almost 1 billion pound cushioning market and its share of this market is valued at over $100 million on the retail level (5). However, over the past several years cotton's share of this valuable market has been decreasing at the rate of 1 percent per year. This decline has not been evenly distributed throughout cotton batting's markets. Today cotton batting comprise only 20 percent of the furniture cushioning market. Cotton holds 60 percent of the automotive market and has managed to retain about 85 percent of the mattress business.

The decrease in use of cotton batting can be almost wholly attributed to competition from polyurethane foam. Polyurethane exhibits outstanding recovery from compressive loadings, even under conditions of high relative humidity, and, in addition, shows vastly improved tensile strength when compared with cotton batting.

It has been obvious for some time that improvements in the performance characteristics of cotton batting would be needed to enable it to compete with polyurethane foam. In 1961, under cosponsorship with various trade associations, SURDD began research with this goal in mind. Cotton Flote, a resinated cotton batting with improved resilience and tensile strength, was the product that evolved from this research endeavor (1). The process consists of spraying a mixture of thermosetting and thermoplastic resins onto the cotton in web form; followed by lapping, drying, and curing. That this product meets the needs of the batting industry is attested to by the fact that a dozen plants are producing an estimated 80 million pounds of Cotton Flote. The automotive industry uses virtually all of this product. Capital requirements prohibit small manufacturers of batting, who supply the furniture and mattress industries, from producing Cotton Flote at this time. Thus, little, if any, of the improved resinated cotton batting is available to furniture and mattress manufacturers.

With the passage of the Highway Safety Act and the amendments to the Flammable Textiles Act, it seems that yet another property must be imparted to cotton batting. That property is flame retardance. Whether used in furniture,

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[1/] A cooperative research undertaking jointly sponsored by the Textile Fibers and By-Products Association, The National Cottonseed Products Association, The National Cotton Batting Institute, the Foundation for Cotton Research and Education, and the Agricultural Research Service, USDA. The research is also indirectly sponsored by the National Association of Bedding Manufacturers, through special contributions to the National Cotton Batting Institute for use in this research effort.

automobiles, or mattresses, flame-retardant cotton batting will safeguard the consumer.

We have succeeded in imparting flame-retardancy to Cotton Flote (2). We have found inexpensive flame retardants applicable from a water system, compatible with currently used chemicals, and easily sprayable. Flame-retardant Cotton Flote has already been used commercially in an inner-spring mattress.

Approximately 90 percent of the cotton batting manufacturers account for less than 50 percent of the total batting production. These small plants cannot afford the capital expenditures necessary to produce Cotton Flote. Some means needs to be found to enable them to manufacture flame-retardant conventional batting by a process separate and distinct from the Cotton Flote system. It is in this particular area that our current research effort is concentrated.

The requirements for the application of flame-retardant characteristics to conventional cotton batting are considerably different than those that apply to the Cotton Flote system, although many of the same chemical compounds can be expected to do the job effectively. For example: In the Cotton Flote process, the bonding of fibers at points of contact is a desirable characteristic that assists in achieving the tensile strength, dimensional stability, and integrity of the products. In addition, the presence of the thermoplastic resin which serves as the bonding agent makes the removal of the flame-retardant chemicals more difficult at high relative humidity and even under conditions of mild leaching. Furthermore, all of the needed chemicals are applied in an operation already incorporated into the process, in a situation where the fibers are in an open array and readily accessible to the treating formulation.

There seems to be no really good place to apply the flame-retarding chemicals to the fibers during normal mechanical processing. For this reason it appears that, at least for the present, our research should be directed toward pretreatment of the fibers before any mechanical processing is undertaken.

Some of the criteria that the flame-retardant treatment must meet are:

1. Inexpensive.
2. Easy to apply.
3. Effective on native linters and textile wastes.
4. Effective at low levels of chemical add-on.
5. Durable to mild leaching, high humidity, and temperature.
6. Odor free after drying and curing.
7. Effective in reducing afterglow.
8. Physiologically inactive.

The first item is, of course, of prime importance in a finished batting product that is expected to sell for 20 to 40 cents per pound. There are a number of chemical compounds that are known to do an excellent job of rendering cotton flame retardant. Among these are tetrakis(hydroxymethyl)-phosphonium chloride (THPC), tris(1-aziridinyl)-phosphine oxide (APO), and tris(2,3 dibromopropyl)phosphate. These chemicals sell for approximately $1 per pound and add-ons of 10 percent or more are needed. As a consequence, their use in cotton batting is obviously uneconomical. Our choice of flame-retardants is broadened, however, by the fact that in this application the flame-retardant need not be durable to multiple laundering.

The second item deals with the application of the chemicals. Ease of application can be interpreted in a number of ways: (1) the mechanical system that might be most appropriate, (2) the chemical system and its particular requirements, (3) the handling of the fibers during treatment and subsequent drying or curing, or both, followed by the storage of the treated fibers. For our experimental purposes, we have limited ourselves to the use of water-based chemical systems using immersion followed by squeeze rolls to bring the wet pickup to the predetermined level. Alternative approaches to be considered in the near future include immersion followed by centrifugation, and pressure impregnation during immersion followed by appropriate dewatering techniques.

The next item states that the treatments we are seeking should be effective on the cotton fibers as they are received. Stated another way, we want to avoid the necessity of preprocessing the linters and textile wastes to remove waxes, pectins, oils, and other extraneous materials.

Next we want to achieve effective flame retardancy at low levels of chemical add-ons. This obviously keeps costs down while at the same time minimizes adverse effects on normal batting properties.

The last four items deal with properties that the treated fibers must exhibit if the products are to be accepted by the consumer. Durability of flame retardancy for cotton batting products is important because cotton batting products are used in many and varied environmental conditions. Consequently, the products must retain their flame-retardancy characteristics under conditions of high temperature, high humidity, and even mild leaching.

Obviously the products must also be odor free, inhibit afterglow, and be physiologically inactive.

The following are some of the things that the treatment must avoid if product performance is to be maintained.

1. Be deliquescent.
2. Reduce quality of webs produced.
3. Significantly increase fly during garnetting.
4. Affect the moisture absorption-desorption of fibers.
5. Affect the air permeability of the array.
6. Dust or powder off the fibers.

The chemical used should not be deliquescent. The treatment must not reduce web quality or increase fly during garnetting. In other words, fiber embrittlement must be kept at a minimum. To preserve the comfort factors of cotton batting the treatment must not significantly affect the natural moisture equilibrium of the fibers nor adversely affect the air permeability of the array. Finally, the treatment must not dust off after mechanical processing.

Tables 1 and 2 give typical flame-retardant formulations and resilience characteristics. For all of the samples we will discuss, the treating formulations were applied by padding picker lap using two dips and two nips and achieving a wet pickup of approximately 100 percent. All retardants were run at various concentrations and the concentrations shown here are those which consistently passed our flame-retardancy tests.

Table 1. — Flame-retardant formulations and resilience characteristics

	Sample A	Sample B	Control
Flame retardant	MAP	NABOR	--
Percent by weight	12.0	10.3	--
Recovery percent:			
70° F.—65 pct. R.H.	79	81	86
80° F,—100 pct. R.H.	82	56	58
Percent compression	76	78	81

Table 2. — Flame-retardant formulations and resilience characteristics

	Sample			
	D	E	F	G
Flame retardant	BAP	DCY-P	PAP	UP
Percent by weight	7.5	8.1	10.1	5.3
Recovery percent:				
70° F.—65 percent R.H.	92	75	83	79
80° F.—100 pct. R.H.	50	57	66	64
Percent compression	78	78	74	75

Sample A is monoammonium polyphosphate at a 12 percent add-on; while Sample B is sodium borate at a 10.3 percent add-on. Notice that the recovery from cyclic loading after 4 minutes for both Samples A and B are quite close to that of the control.

Table 2 lists four additional flame retardants and their recovery performance. Sample D is described as a borated amido polyphosphate and has a 7.5 percent add-on. Sample E is the reaction product of dicyandiamide and phosphoric acid. It was methylolated to improve its shelf life and solubility. Sample F is propyl ammonium phosphate tried at 10.1 percent add-on. Finally, Sample G is a urea-phosphate complex at 5.3 percent add-on. Notice that the resilience characteristics of all samples are quite satisfactory.

So far, we've been speaking of properties other than the most essential one--flame-retardance. Next, we will present data representing our attempt to measure this critical property. Because there are no guidelines as to what might constitute an acceptable level of flame retardancy in mattresses, furniture, or automotive seats, we have had to establish our own tentative standards for screening purposes. They are:

1. Afterflame less than 5 seconds.
2. Afterglow less than 5 seconds.
3. Overall char length less than 15 centimeters.
4. Main char length less than 10 centimeters.

Cotton batting can be expected to be exposed to a variety of environmental conditions; therefore, we have conditioned our samples in four different environments before testing:

1. 70° F. and 65 percent R.H. for 24 hours.
2. 100° F. and 100 percent R.H. for 72 hours.
3. 158° F. for 16 hours.
4. Water saturation followed by drying at 158° F. for a minimum of 16 hours.

The flame retardancy of the samples was measured using a modification of the AATCC Test Method 34-1966 (Fire Resistance of Textile Fabrics). This test involves hanging a sample 2 inches wide by 10 inches long vertically over a bunsen burner. Samples are usually 1 inch thick. The flame from the bunsen burner is 1½ inches high and the sample is adjusted to project three-fourths inch into the flame. The flame burns for 12 seconds. We measure the time that the flame persists after the bunsen burner is extinguished, and the time that the red afterglow persists. We also measure the length of the main charred area at the bottom of the sample and the overall char length including scorch from flashing. By these measurements, we are able to differentiate between the effectiveness of a number of treatments to the point where we can, with reasonable confidence, select samples having different degrees of flame retardancy.

It should be recognized that cotton batting cushions are usually used in an assembly where they are protected by a covering of fabric, and that the test results that are obtained on the cotton batting component do not necessarily carry over to the finished mattress, furniture, or automobile seat.

Table 3 shows data of Sample A, 12 percent monoammonium polyphosphate, and Sample B,

Table 3. — Flame-retardancy characteristics

	Sample		
	A	B	Control
70° F.—65 pct. R.H.:			
Afterflame (sec.)	0	1	B.
Afterglow (sec.	0	4	E.[1]/
Overall char (cm.)	3	2	L.—/
Main char (cm.)	2	1	
100° F.—100 pct. R.H.:			
Afterflame (sec.)	0	0	B.
Afterglow (sec.)	0	12	E.[1]/
Overall char (cm.)	2	3	L.—/
Main char (cm.)	1	2	

[1]/ Burned entire length.

10.3 percent sodium borate. The 12 percent add-on of MAP was adequate in tests conducted after conditioning at 70° F.-65 percent R.H. and at 100° F. and 100 percent R.H. However, notice the performance of the sodium borate sample. Even under standard laboratory conditions it shows a distinct propensity to afterglow. The importance of suppressing afterglow cannot be over emphasized. It is the afterglow that causes the control sample to burn its entire length. After the source of ignition is removed, the control shows little if any afterflame. However, the hot glow persists and propagates from fiber to fiber giving off large volumes of noxious

fumes. This mechanism continues until the entire sample is charred. Additionally, the afterglow is extremely hot, even hotter than the flame itself, and can cause severe burns to anyone coming in contact with the glowing cotton. At 100° F. and 100 percent R.H., Sample B shows even greater afterglow. This is not a desirable trend, but not unexpected since the borates generally lack good hydrolytic stability.

Table 4 shows Samples A and B after conditioning at 158° F. and also after being saturated

Table 4. — Flame-retardancy characteristics

	Sample		
	A	B	Control
158° F.—16 hr. (dry):			
Afterflame (sec.)	0	0	
Afterglow (sec.)	0	0	B
Overall char (cm.)	3	2	E. [1]/
Main char (cm.)	2	1	L.—/
158° F.—16 hr. (wet):			
Afterflame (sec.)	0	0	
Afterglow (sec.)	0	30.0	B.
Overall char (cm.)	4	5	E. [1]/
Main char (cm.)	3	3	L.—/

[1]/ Burned entire length.

with water. Once again the monoammonium polyphosphate performs quite well. Also, the lack of hydrolytic stability on the part of sodium borate is further evidenced when tested after water saturation. Here afterglow persists for 30 seconds. These data indicate that the use of sodium borate and probably other borates as well, would have to be restricted to uses where hydrolytic stability is not a factor.

The possibility of combining a phosphorus-containing flame retardant with one containing boron was investigated as a means of mitigating the above problem. Sample D in tables 5 and 6, a borated amido polyphosphate, is an attempt to prove whether this combination may be beneficial. Table 5 shows that at 70° F., 65 percent R.H. there is no afterglow, and also at 100 percent R.H. there is only 1 second afterglow.

Table 5. — Flame-retardancy characteristics

	Sample			
	D	E	F	G
70° F.—65 pct. R.H.:				
Afterflame (sec.)	0	0	0	0
Afterglow (sec.)	0	0	0	0
Overall char (cm.)	2	6	4	7
Main char (cm.)	1	2	2	2
100° F.—100 pct. RH. (3 days):				
Afterflame (sec.)	0	0	0	0
Afterglow (sec.)	1	0	0	0
Overall char (cm.)	1	6	3	8
Main char (cm.)	1	2	2	2

Table 6. — Flame-retardancy characteristics

	Sample			
	D	E	F	G
158° F.—16 hr. (dry):				
Afterflame (sec.)	0	0	0	0
Afterglow (sec.)	2	0	0	0
Overall char (cm.)	1	6	2	8
Main char (cm.)	1	2	2	2
158° F.—16 hr. (wet):				
Afterflame (sec.)	0	0	0	0
Afterglow (sec.)	1	0	0	0
Overall char (cm.)	3	4	5	4
Main char (cm.)	1	2	2	3

Apparently sufficient phosphorus is present to enable the product to perform satisfactorily at 100 percent R.H. Samples E, F, and G are all phosphorus-containing compounds. These samples perform well both at 65 percent R.H. and 100 percent R.H. Table 6 gives the results after exposure to 158° F. for 16 hours and after saturation and drying for Samples D, E, F, and G. Once again, all samples performed satisfactorily. We feel that these formulations would produce flame-retardant cotton batting which would be durable under its usually encountered environmental conditions.

We have also examined the use of the Methenamine Timed Burning Tablet as a means of simulating a burning cigarette as a source of

ignition. This test is used quite frequently in evaluating mattress products. The methenamine tablet is placed in the center of the sample and ignited by touching a match carefully to the edge of the tablet so as not to contact the surface of the batting. The ignition flame and any propagated flame is allowed to burn to completion. The maximum diameter of the charred area is measured to the nearest tenth of an inch. We found that this test is not very sensitive. Not only was it impossible to measure the effect of flame-retardant concentration, but it was even difficult to notice much difference in afterflame or afterglow for a myriad of different flame retardants applied at many levels. We feel that this may be due to the fact that the temperature at the cotton/flame interface is only 200 to 250° C. and the char formed provided sufficient insulative properties to prevent further degradation. The hot part of the flame, approximately 400° C., was in the atmosphere above the sample. In the vertical test, on the other hand, the hottest part of the flame impinges on the cotton, and this temperature is apparently greater than the minimum needed for adequate treatment differentiation. For this reason we place primary reliance on the vertical test for screening purposes.

To obtain a fuller understanding of possible mechanisms for fire retardancy and differences that may exist between various types of flame retardants, we are investigating the use of thermoanalytical techniques. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have found quite extensive use in recent years in the study of materials as they undergo chemical and physical changes during heating.

The DTA analyses were performed on the DuPont 900 differential thermal analyzer and TGA on the DuPont 950 thermogravimetric analyzer. The DTA consists of a cell assembly, temperature programmer, amplifier and X-Y plotter. Glass beads were used as a reference material. The temperature difference between the sample and the reference material forms the Y axis while the sample temperature is the X axis. In all the work described here the heating rate was 30° C./minute. This rapid heating rate produces a larger ΔT and sharper peak than slower heating rates. In addition, it must be remembered that the sample temperature at which the endotherm or exotherm occurs is dependent upon the heating rate; that is, the faster the heating rate, the higher the sample temperature will be when the deviation from the baseline occurs. The samples used for DTA were prepared by grinding in a Wiley mill to pass through a 20-mesh screen. Approximately 10 mg. samples were placed in a 4 mm. capillary tube. The chromel-alumel thermocouple was inserted through the top of the tube and centered in the sample by means of a ceramic sleeve. A glass head reference was prepared in a similar manner. Sensitivity was 1° C./inch and the test conducted in air flowing at two standard cubic feet per hour.

Thermogravimetric analyses were performed on 5 mg. samples. This was the maximum sample size that the tared aluminum weighing pan would accommodate without interfering with the chromel-alumel thermocouple which was centered 1 mm. above the sample. The heating rate was 30° C./min., sensitivity was 1 mg./inch and the tests conducted in air.

Figures 1 and 2 show the differential thermographs for the six flame retardants under study plus scoured and bleached cotton and untreated control batting. The first endotherm for all samples results from the loss of moisture which begins near 100° C. The first point of real interest in figure 1 is a comparison of the thermographs for scoured and bleached fibers and the untreated control battings. The scoured and bleached sample shows a strong endotherm at 370° C. while the untreated batting shows a weak exotherm beginning at 375° C. This difference in thermal behavior might be accounted for if it is remembered that a given thermograph is quite often the result of competing reactions; that is, an exothermic and endothermic reaction occurring simultaneously with the thermograph recording the algebraic sum. Thus, the control sample with its waxes, pectins, protein, and possible cations present possibly has a large enough exothermic reaction in the same temperature range to effectively cancel the endotherm of the cellulose itself. Mack and Donaldson (3), in their study of the effects of bases on the pyrolysis of cellulose, find that with as little as 0.3 percent sodium hydroxide present on cellulose, this same phenomenon occurs.

BAP and sodium borate, both boron containing flame retardants, continue the effect

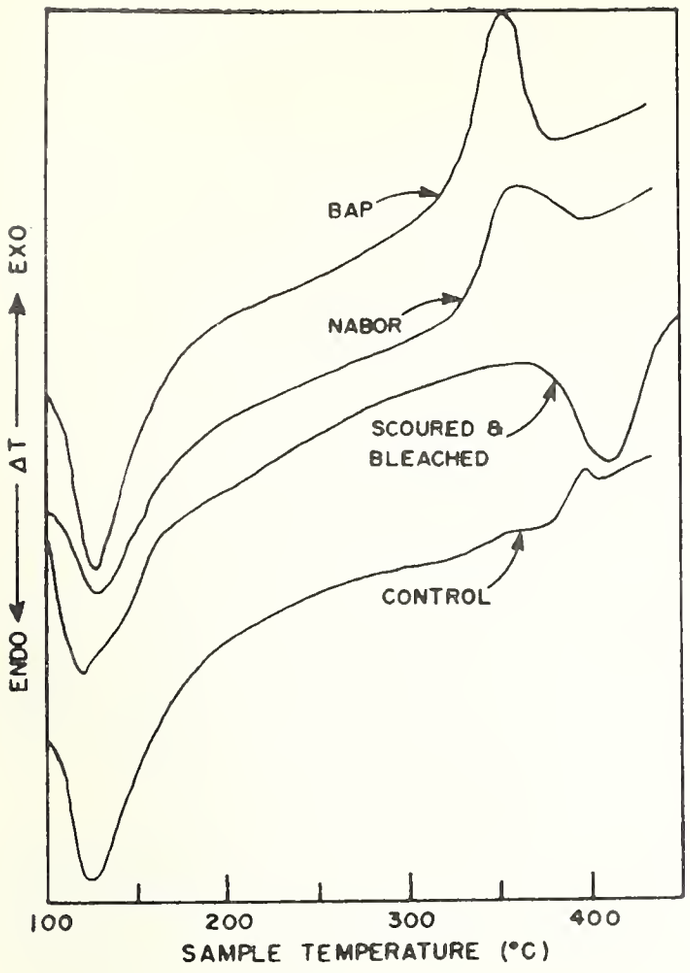

Figure 1. — DTA in air (heating rate = 30° C./ min.)

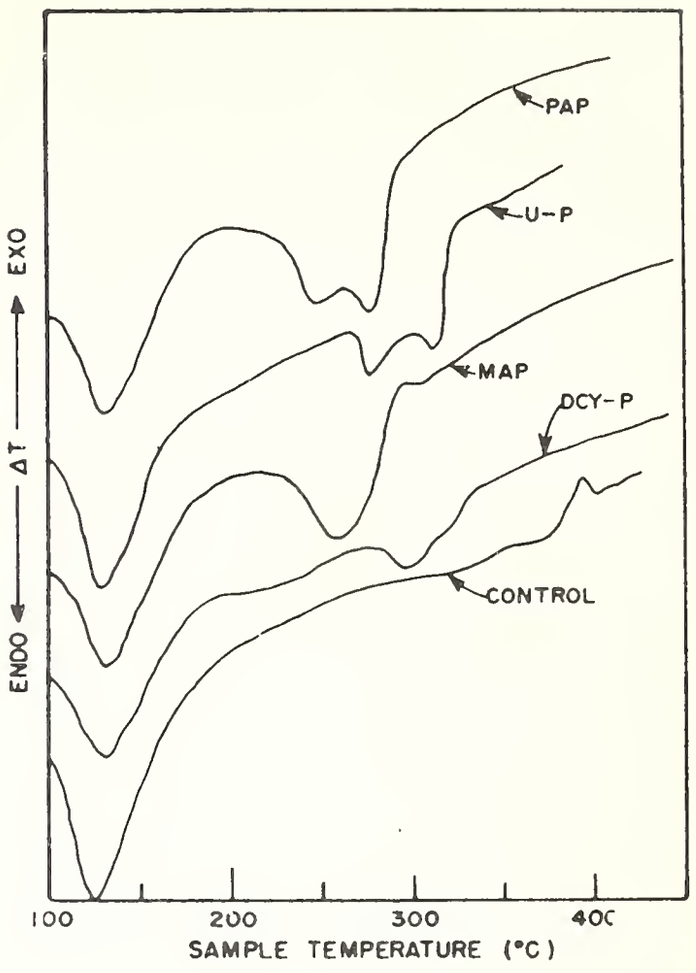

Figure 2. — DTA in air (heating rate = 30° C./ min.)

noted in the untreated batting. The exothermic effects are larger and occur at slightly lower temperatures, 345° C. for BAP and 350° C. for sodium borate.

Figure 2 shows the thermographs of the phosphorus-containing flame retardants and the control for comparison. In each instance, the thermographs are characterized by endotherms that occur at temperatures below that of the control. Schuyten and others stated that many effective flame-retardant treatments acted essentially as Lewis acids, which were capable of catalytic activity which changes both the course and speed of reaction (4). Each of the four thermographs lends itself to such an interpretation. The PAP and urea-phosphate samples are especially interesting. Each shows the overlapping of two endotherms. TGA results, which will be discussed in detail later, help interpret this occurrence. The first endotherm for propyl ammonium phosphate begins at about 215° C. TGA data show that this is before any major sample weight loss. Thus, perhaps this first endotherm is caused by the decomposition of the flame-retardant which then exerts a catalytic effect upon the cellulose decomposition. The onset of the second endotherm at 265° C. corresponds to the beginning of sample decomposition as revealed by TGA. Similar changes appear to occur in the sample treated with urea-phosphate. The occurrence of the first endotherm at 265° C. does not correspond to any major weight loss; however, the onset of the second endotherm at 300° C. corresponds to the initiation of sample decomposition. Monoammonium phosphate and DCY-phosphoric acid samples each show only one endotherm and the

onset temperature of the endotherm corresponds to the initiation of decomposition.

Figures 3 and 4 show the results of thermogravimetric analyses. Notice in figure 3 the vast difference in percent residue between the scoured and bleached fibers and control batting which is composed of unscoured and unbleached linters and textile waste. This difference was suggested by the DTA results. At 425° C. the control has 32 percent residue while the scoured and bleached sample yields only 10 percent residue. The decomposition temperature of the control is about 30° lower than the scoured and bleached sample (316° C. versus 348° C.). Sodium borate and DCY-phosphoric acid flame retardants have approximately the same decomposition temperature as the control. Both show slightly increased residues.

Figure 4 shows TGA results for the other four flame retardants. BAP began decomposition around 320° C. the same as the control, and yielded 38.4 percent residue. PAP, or propyl ammonium phosphate, began decomposition at 258° C. and yielded 39.6 percent residue. The onset of decomposition of the urea-phosphate sample was at 293° C. and yielded a residue of 42.0 percent. Finally, the monoammonium phosphate sample began decomposition around 245° C. and yielded a char of 55.5 percent.

Conventional cotton batting doesn't have a great deal of tensile strength. A sample of 2.0 lb./ft.^{3} density may have 3.0 pounds to break in the machine direction and 1.5 pounds transverse to the machine direction. Obviously then, a flame-retardant treatment must not further lower this already poor tensile strength. Figure 5 gives the tensile strength of Samples D, E, F, and G expressed as a percent of the control. This test is a Grab breaking strength performed on an Instron with 1 inch per minute cross-head speed and 10 inches per minute chart speed. Sample E shows the greatest loss of tensile strength. This may be caused by free formaldehyde remaining in the formulation after methylolation and which subsequently crosslinked the fibers and embrittled them. Samples D and G also exhibit a loss of tensile strength but not to the extent of Sample E. Sample F, with propyl ammonium phosphate, showed tensile strength slightly greater than the control. The fact that the loss is generally greater, transverse to the machine direction indicates that part of the loss is attributable to fiber breakage during mechanical processing.

Figure 6 gives another indication of increased fiber embrittlement. In this case it is the increase of fly during garnetting. Fly is the term given to the short, sometimes broken fiber fragments which are thrown out of the garnett during mechanical processing. Even though this fly is collected and some is fed back into the garnett, there is a law of diminishing returns; that is, if too much fly is fed back very poor product quality results and an even greater percentage of fly is generated. The manufacturers have a vital economic concern for any fiber treatment that may embrittle fibers. Notice that there is an inverse relationship between fly and tensile strength. Sample E, which had the lowest tensile strength, generated the greatest amount of fly. Sample F, which had the greatest tensile strength, has the least amount of fly. Thus, increased fly indicates increased fiber breakage and leads to decreased tensile strength.

One possible means of attacking this problem is through the use of lubricants or softeners in the treating formulation. The textile industry has been known to resort to such measures on occasion. We have begun such an investigation and figure 7 shows promising results. We selected Sample E as the control, since it showed the greatest fiber damage. (Fly 20 percent greater than the control.) In this case, a commercially available polyethylene emulsion was used as the softener. Thus, formulations containing 8.1 percent of the dicyandiamide phosphoric acid flame retardant and 1.7 and 2.5 percent polyethylene were used to treat the rawstock. At the 1.7 percent level the fly increase was halved and with 2.5 percent of polyethylene softener present the fly was practically the same as the control. These results, though based on limited tests, indicate that softeners are indeed a means of reducing fiber breakage. We are conducting additional tests with other classes of softeners and lubricants to determine the most efficient and economical treatment.

To date, our research has raised as many questions as it has answered. But this is an on-going effort and we are presently seeking answers to the unsolved problems. We do believe

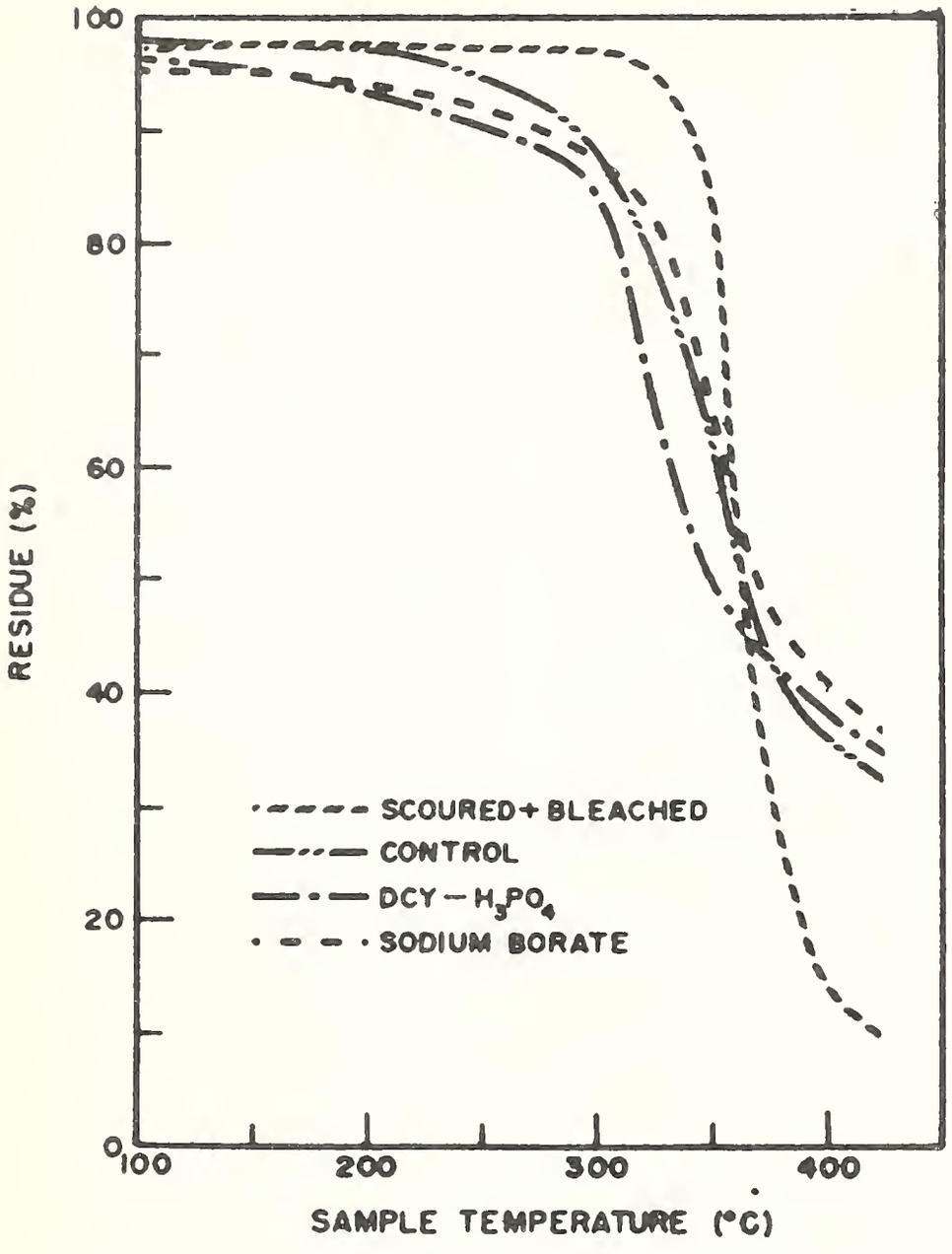

Figure 3. — TGA in air (heating rate = 30° C./min.)

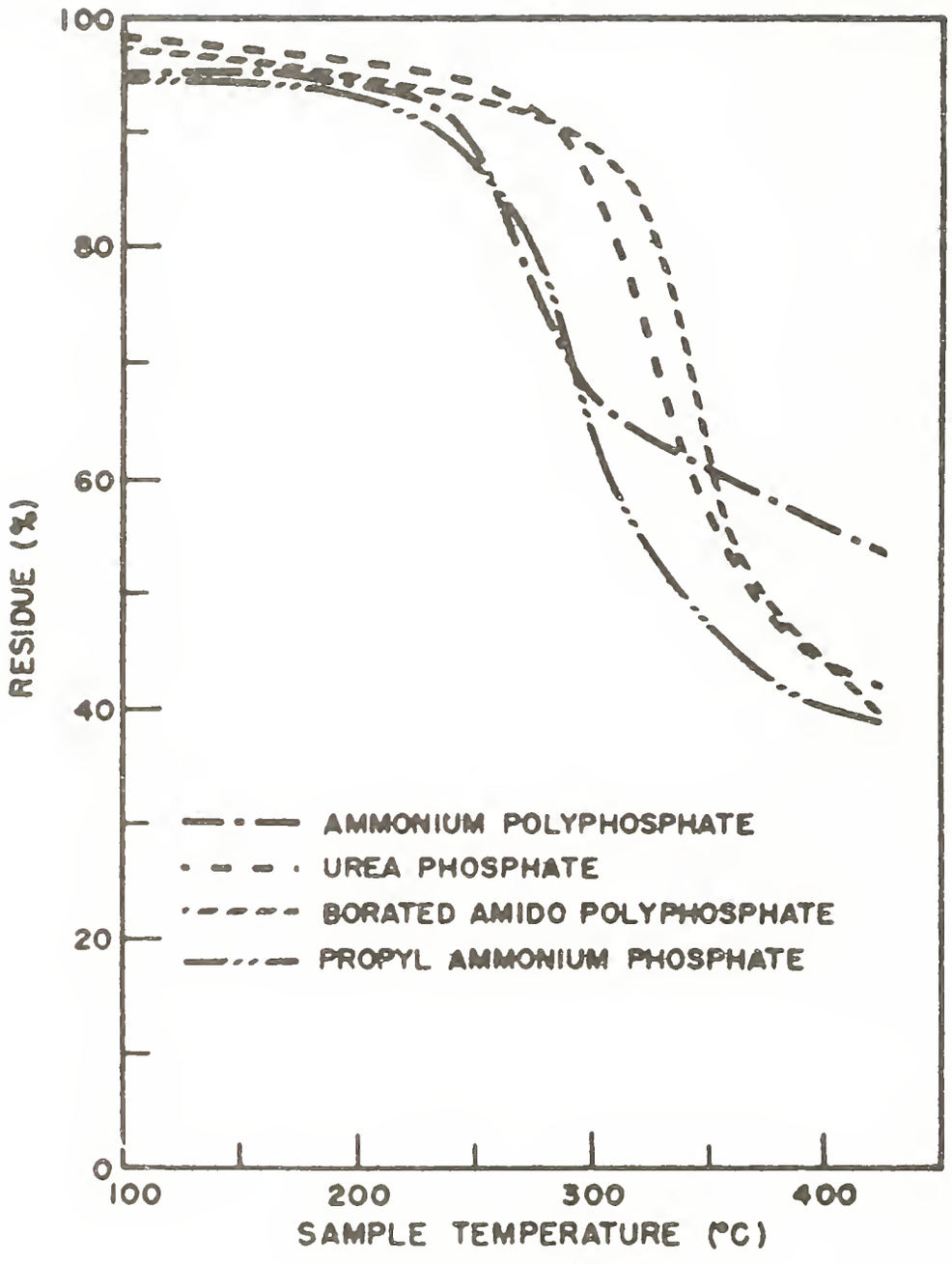

Figure 4. — TGA in air (heating rate = 30° C./min.)

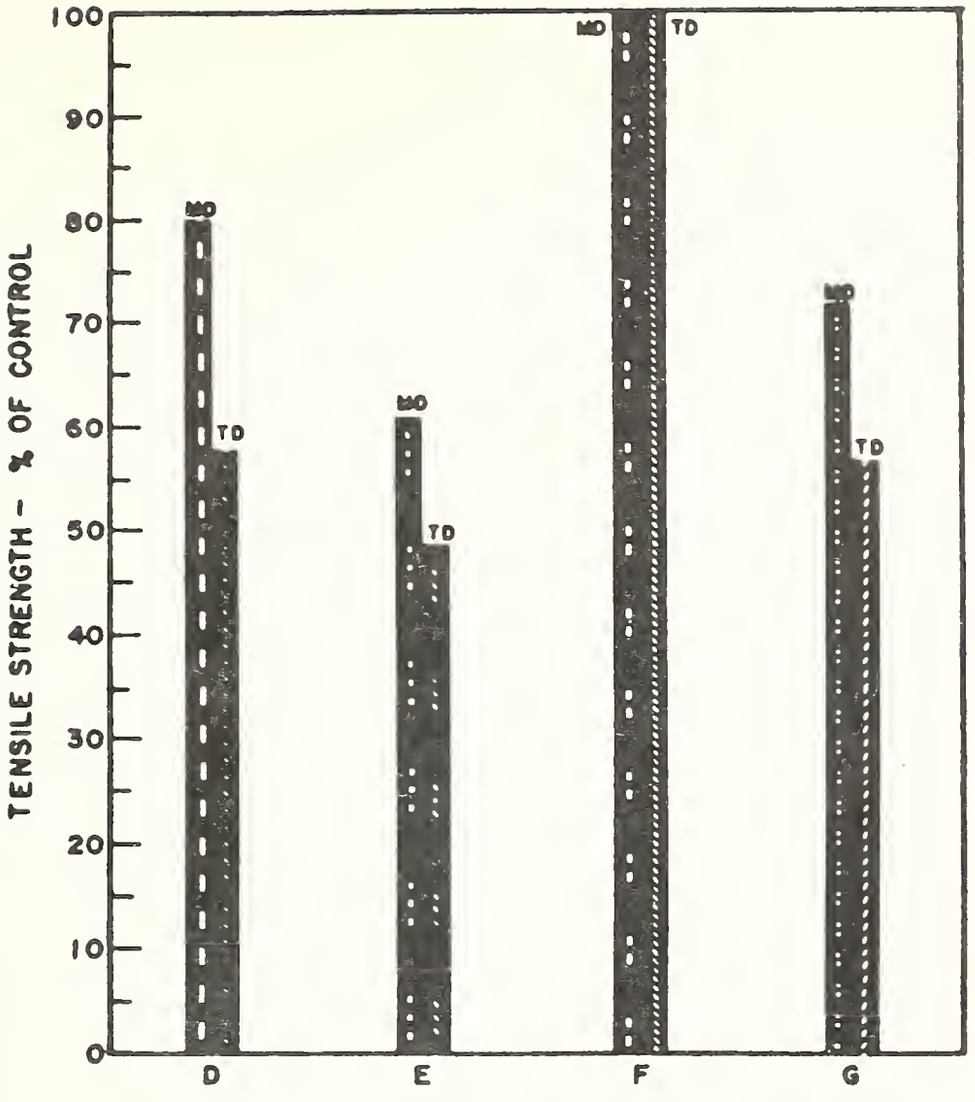

Figure 5. — The effect of flame retardant on tensile strength.

that from the data presented, it can be concluded that there are a number of chemical systems that will confer a significant degree of flame retardancy to cotton batting. These chemicals for the most part meet the criteria of permanency; that is, they resist removal by elevated temperature, mild leaching, and high relative humidity. Results of thermal analysis showed flame retardants lowered the active combustion temperature and increased the yield of char.

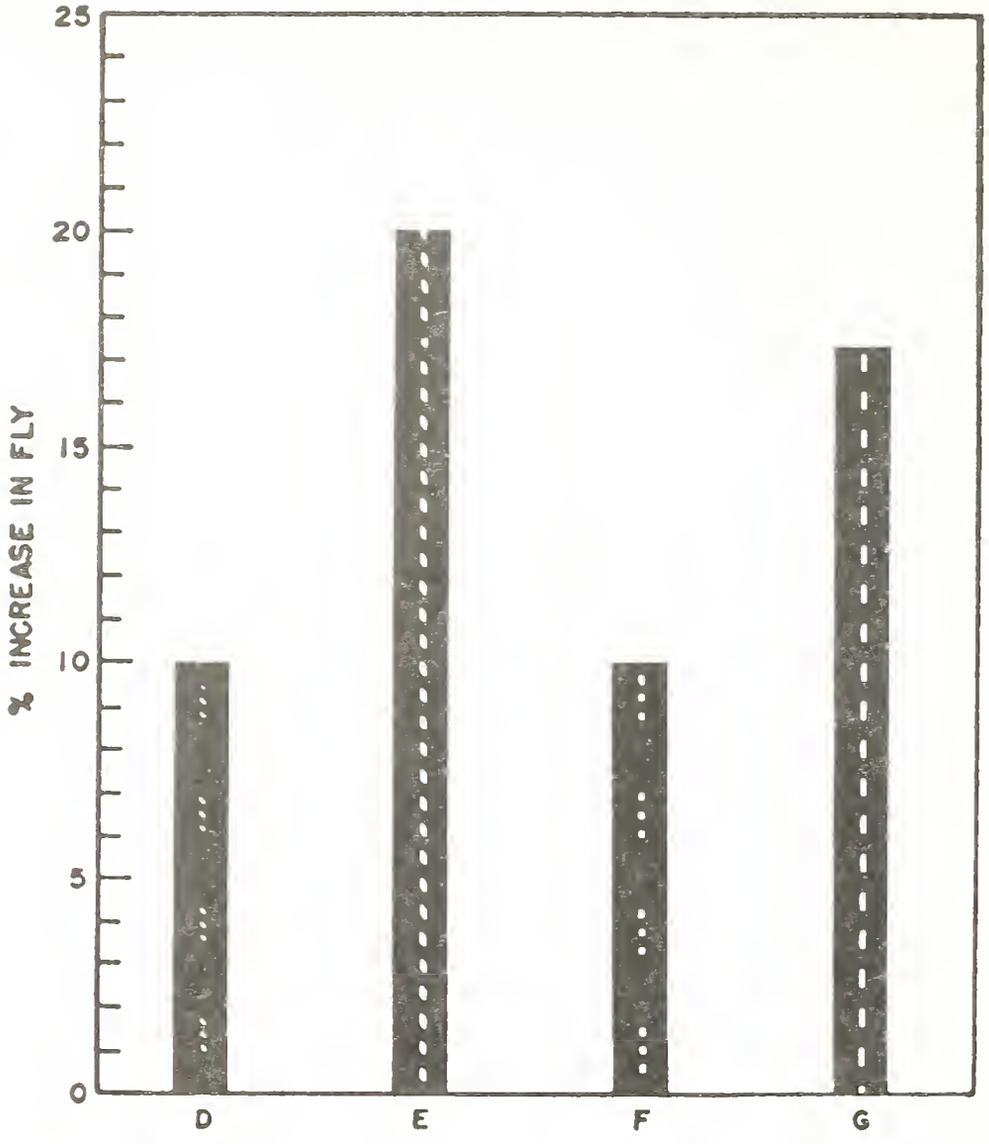

Figure 6. The effect of flame retardant on garnettability.

It appears that the problem of fiber embrittlement can be economically overcome through the use of lubricants or softeners.

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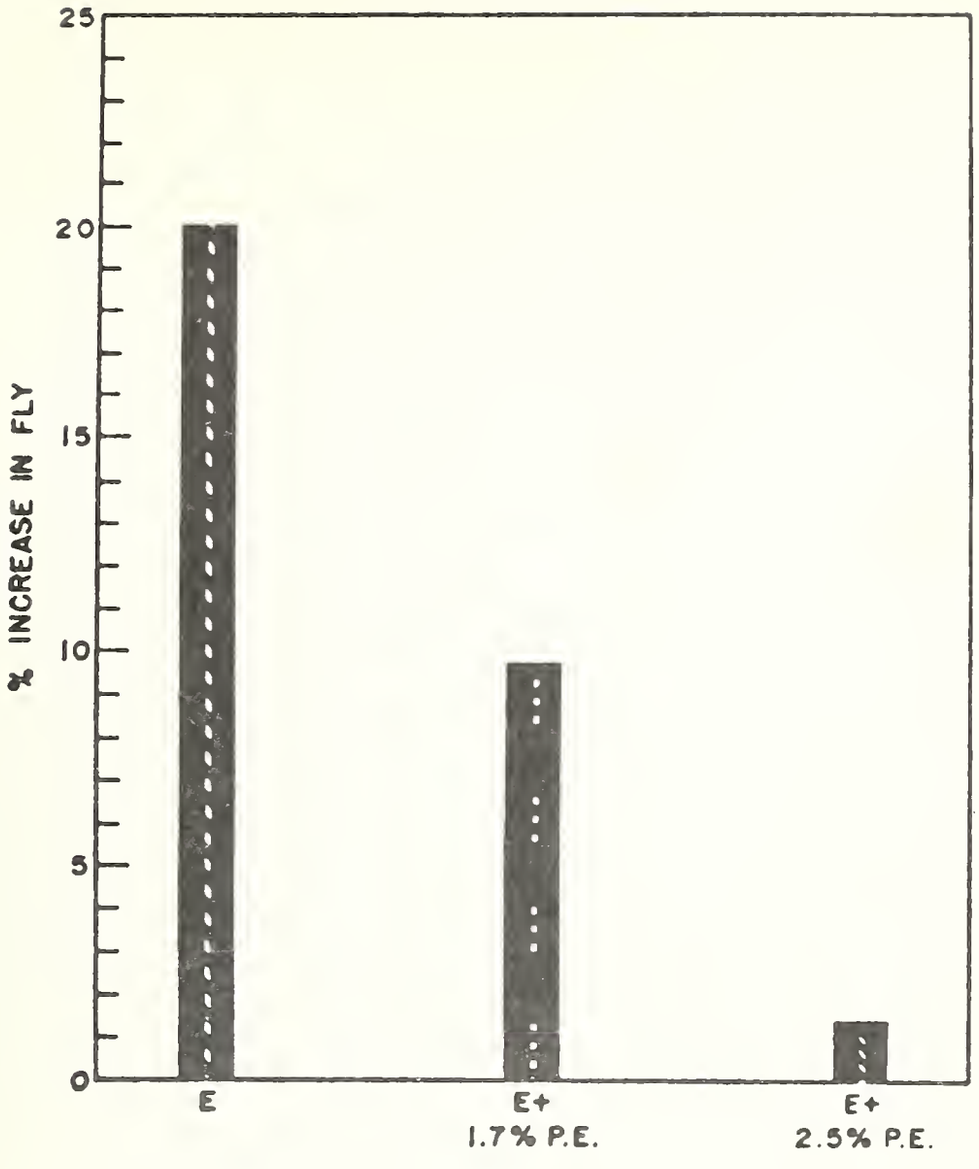

Figure 7. -- The effect of softeners on garnettability.

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